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CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

	PAGE
I.—Nitrites of the Alicyclic Ammonium Series. Nitrosopiper- azinium Nitrite. By PRAFULLA CHANDRA RAY and JITENDRA NATH RAKSHIT	1
II.—Chlorides of the Mercurialkyl- and Mercurialkylaryl- ammonium Series and their Constitution as based on Conduc- tivity Measurements. By PRAFULLA CHANDRA RAY and NILRATAN DHAR	3
III.—Equivalent Conductivity and Ionisation of Nitrites. By PRAFULLA CHANDRA RAY and NILRATAN DHAR	10
IV.—Viscosity and Association. Part III. The Existence of Racemic Compounds in the Liquid State. By FERDINAND BERNARD THOLE	19
V.—The Formation of Tetrahydro-oxazoles from α -Hydroxy- β -anilino- $\alpha\beta$ -diphenylethane and its Homologues. By HORACE LESLIE CROWTHER and HAMILTON McCOMBIE	27
VI.—The Action of Halogens on Silver Salts. By HUGH STOTT TAYLOR (1851 Exhibition Scholar, University of Liverpool).	31
VII.—Diphenylene. Part II. By JAMES JOHNSTON DOBBIE, JOHN JACOB FOX, and ARTHUR JOSIAH HOFFMEISTER GAUGE	36
VIII.—Synthetical Aminoglucosides Derived from <i>d</i> -Glucos- amine. By JAMES COLQUHOUN IRVINE and ALEXANDER HYND, M.A., B.Sc. (Carnegie Fellow).	41
X.—The Condensation of α -Keto- β -anilino- α -phenylethane and its Homologues with Carbonyl Chloride, Phenylcarbimide, and Phenylthiocarbimide. By HAMILTON McCOMBIE and HAROLD ARCHIBALD SCARBOROUGH	56

	PAGE
X.—Studies in the Camphane Series. Part XXXIII. Orientation of Tiemann's <i>iso</i> Aminocamphor. By MARTIN ONSLOW FORSTER and HUBERT ARTHUR HARRY HOWARD	63
XI.—The Constitution of the <i>ortho</i> Diazoimines. Part II. The <i>p</i> -Tolyl- β naphthatriazoles. By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT	7
XII.—Co-ordination Compounds of Vanadium. Part I. The Acylacetates. By GILBERT T. MORGAN and HENRY WEBSTER MOSS, A.I.C., A.R.C.Sc.I.	78
XIII.—Chemical Reactivity and Absorption. Part II. The Variation of Absorption with Concentration. By EDWARD CHARLES CYRIL BALY and FRANCIS OWEN RICE	91
XIV.—The Constitution of Cytisine, the Alkaloid of <i>Cytisus laburnum</i> . Part I. The Synthesis of α -Cytisolidine and of β -Cytisolidine. By ARTHUR JAMES EWINS	97
XV.—The Synthesis of Some New Dimethyltetrahydroquinolines. By ARTHUR JAMES EWINS and HAROLD KING	104
XVI.—Optically Active Glycols Derived from the Phenyl lactic Acids. Part I. By ALEX. MCKENZIE and GEOFFREY MARTIN	112
XVII.—Dibenzyl- and Diphenyl-silicols and -silicones. By GEOFFREY MARTIN	115
XVIII.—The Photography of Absorption Spectra. By THOMAS RALPH MERTON, B.Sc.(Oxon)	121
XIX.—The Relation between Viscosity and Chemical Constitution. Part VI. Viscosity an Additive Function. By ALBERT ERNEST DUNSTAN and FERDINAND BERNARD THOLE	127
XX.—The Relation between Viscosity and Chemical Constitution. Part VII. The Effect of the Relative Position of Two Unsaturated Groups on Viscosity. By ALBERT ERNEST DUNSTAN, THOMAS PERCY HILDITCH, and FERDINAND BERNARD THOLE	131

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:—

PART I.

Organic Chemistry.

	PAGE
BADISCHE ANILIN- & SODA-FABRIK. Preparation of Δ^2 -Butadiene and its Homologues	i, 1
BADISCHE ANILIN- & SODA-FABRIK. Preparation of Isoprene	i, 1
FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. Preparation of β -Dimethylethylene	i, 1
SCHLEENZ (HERMANN). The History of Distillation and of Alcohol	i, 2
FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. Preparation of Homologues of Phinacene	i, 2
FRANKE (ADOLF) and O. KIENBERGER. The Formation of Polycyclic Rings	i, 2
KARVONEN (A.). Halogen Ethers	i, 2
SCHUECKE (RUDOLF) and A. HOCHSTETTER. Preparation of Carbonic Esters	i, 4
MERCK (EMANUEL). Preparation of Halogen Foricyl Esters	i, 5
CHEMISCHE FABRIK AUF AKTLEN VORM. E. SCHERING. Preparation of Esters of Butenol	i, 5
FRAGER (W.). The Mercury Compounds of Ethyl Nitroacetate	i, 5
BOESKEN (JACOB) and MEYER CLUWEN. Action of Aluminium Chloride on Acetic Anhydride	i, 6
REYCHLER (ALBERT). Soaps	i, 6
PALOMAA (MAATI H.). Dissociation Constants of Aliphatic Hydroxy- and Alkoxy-acids	i, 6
CRNOJA (MIL. A.). Action of Magnesium Methyl Iodide and Bromide on Di- α -bromoisopropyl Ketone and on α -Bromo-isopropyl <i>tert</i> -Butyl Ketone (Pentamethyl-moneketone): Synthesis of β -Hydroxypentamethyl- α -valeric Acid and Pentamethylvalerolactone	i, 7
HIMBERG (BROTH). Optically Active Dichlorosuccinic Acids	i, 7
BEREND (ROBERT) and GERHARD TEN DOORNKAAT KOOIJMAN. New Method of Preparation of Malonic Acid	i, 8
JASSIN-BAREND C. P. A. Elucidation of the Constitution of Cholic Acid by Bromination	i, 9
JOLLES (ADOLF). Preparation of the <i>p</i> -Bromo-phenylhydrazine Compound of Glyoxylic Acid	i, 9
GOLDSCHMIEDT (GUIDO) and ELSA ZERNER. The Action of <i>p</i> -Bromo-phenylhydrazine on Glyoxalolactone	i, 9
LEW (OSCAR). The Mechanism of Oxidation Processes	i, 10
FRANKE (ADOLF) and ARTHUR KLEIN. α -Bromomethylpropylaldehyde. II. The Friedel-Crafts Reaction	i, 10
FRATON (VLADIMIR N.). Catalytic Reactions at High Temperatures and Pressures. XXV.	i, 10
BLANKSMA (JAN J.). The System Aceton-phenylhydrazine-Water	i, 11
BLAISE (EDMOND E.). Syntheses by means of Mixed Organocine Derivatives, α -Polychloro ketones. Constitution of the Ordinary Trichloroacetone	i, 11
FAVORSKI (ALEXEI I.) [with P. ASCHMARIN, G. BRITANT, M. CHERNOUSOVA, E. FELDMAN, I. LUTSON, B. ISACHENKO, M ^{re} . L. KOLDOVA, N. MANDRYK, D. SCHOLSKI, (M ^{re} . A. UMNОВА, A. VANSCHLIT, T. VILITSKOVSKI, and (M ^{re} . A. ZACHAROVA.] Action of Halogen Compounds of Phosphorus on Ketones: Bromo-ketones, and Keto-alcohols	i, 12
USSEKIN (P. J. H. VAN). Sugar Solutions and Calcium Hydroxide	i, 16

	PAGE
BERTHELOT (DANIEL) and HENRI GAUDECHON. Photolysis of Sucrose by Ultra-violet Rays	i, 16
LISNET (LEON) and CHARENTIER. Composition of Press Cakes from Sugar Refineries	i, 17
SAMEC (MAX). Plant Colloids. II. The Stability of Starch Solutions	i, 17
STOKLASA (JULIUS), JOHANN SEBOR, and WENZEL ZDOBNIČKÝ. Photochemical Synthesis of Carbohydrates	i, 18
CHANDELON (TH.). Existence of a Hydrate of Nitrocellulose	i, 18
TASSART. A New Nitrocellulose	i, 18
WORDEN (EDWARD C.). Formulated Cellulose	i, 19
SCHMIDT (ERNST) and A. SEEBERG. Neurine Bromide	i, 19
WERNER (ALFRED) and MCCUTCHEON. The Asymmetric Cobalt Atom. VI.	i, 19
WERNER (ALFRED) and YUJI SHIBATA. The Asymmetric Cobalt Atom. VII.	i, 21
WERNER (ALFRED) and G. TSCHERNOV. The Asymmetric Cobalt Atom. VIII.	i, 22
ADERHALDEN (EMIL) and ERICH WURM. α -Aminobutyric Acid and its Derivatives	i, 23
VIQUERAT (ALOIS). Preparation of Creatine from Urine	i, 23
TSCHUGARY (J.), and B. ORLIKINE. Some Complex Compounds of Platinum Chloride with Aminoacetal	i, 23
ZWEIFERGER (NILS VON). The Nitrile and Sulphonamide of Thiodiacetic Acid	i, 24
MILIKAN (J.). Constitution of the Compound known as Phorononitrile, and on Some Other Derivatives of Phoronic and Mesitylic Acids	i, 24
VOUGNASOS (ALEXANDER C.). The Formation of Metallic Nitrides from Thiocyanates and Cyanides	i, 25
HAUSER (OTTO) and E. BRESLSKI. The Supposed Case of Isomerism with Potassium Ferricyanide	i, 26
SCHWARZKOPF (PAUL). Complex Compounds of Iron and the Formation of Nitroprusside	i, 26
ORLOV (N. A.). Preparation and Properties of Scandium Platinocyanide	i, 27
PETTERSON (LIZZIE). Some Metallic Salts and Complex Metallic Derivatives of Cyano-carboxylic Acids and their Esters	i, 27
GEBHARD (KURT). The Benzene Problem	i, 28
SEIDA (HERMANN). Chemical Action of Light. III. Oxidation of Benzene Hydrocarbons	i, 28
KUNCKELL (FRANZ) and GEORG ULEX. Rational Preparation of Benzene Homologues	i, 29
BYGDEM (ARIS). α -Phenyl- β -dimethylpropene, a New Amylbenzene	i, 29
STOBER (HANS) and ERICH REUSS. Influence of Light on the Rate of Polymerisation of Ethylbutadiene	i, 29
ISTRATI (CONSTANTIN I.) and M. A. MIHAILESCU. Action of Aniline on 1:3:5-Tribromo-2:4:6-tri-iodobenzene	i, 29
HOLLEMAN (ARNOLD F.). Rule of the Conservation of the Type in Benzene Substitutions	i, 30
BLANKSMA (JAN. J.). Nitro-derivatives of 2:6-Dibromotoluene	i, 31
FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. Preparation of Anthracenemonosulphonic Acids	i, 31
SCHMIDLIN (JULIUS). Tridiphenylmethyl	i, 32
SCHMIDLIN (JULIUS) and ANTONIO GARCIA-BANUS. Phenylidiphenylmethylmethyl	i, 33
SCHMIDLIN (JULIUS) and ANTONIO GARCIA-BANUS. Reduction of Aromatic Alcohols with Aliphatic Alcohols	i, 34
SCHLENK (WILHELM) [with C. BORNHARDT, ANNA HERZENSTEIN, LEOPOLD MAIR, GEORG RACKY, and JULIUS RENNIG]. Valency of Carbon, Arsenic, and Silicon	i, 34
RADLESS (HANS). Spirans. VI. Some Properties of the Spiran Carbon Atom	i, 37
KOMATSU (SHIGERU). Stereochemistry of Quinquevalent Nitrogen. I. Formation and Decomposition of the Quaternary Ammonium Bases and Salts	i, 39

	PAGE
SENDERENS (JEAN B.) and JEAN ABOULENC. Esters Derived from Cyclanols and Acids of the Formic Acid Series	i, 41
SENDERENS (JEAN B.) and JEAN ABOULENC. Esterification of Cyclanols by Aromatic Acids	i, 42
GUERBERT (MARCEL). Action of Potassium Hydroxide on <i>cyclohexanol</i> ; Synthesis of <i>cyclohexylcyclohexanol</i> and of <i>di-cyclohexylcyclohexanol</i>	i, 42
BOESEKEN (JACOB). Catalytic Action. V. Comparison of the Action of Various Catalysts. III. Acetylation of <i>o</i> -Nitrophenol, Carbazole, and Diphenylamine, and Some Observations on <i>o</i> -Nitroaniline and Tribromophenol as well as their Acetyl Derivatives	i, 43
MAILHE (ALPHONSE). Nitro-derivatives of Diphenylene Oxide and of Phenyl Ether	i, 44
ZINCKE (THEODOR) and OTTO KRÜGER. <i>m</i> -Dithiolbenzene (Dithioresorcinol)	i, 44
ZINCKE (THEODOR) and ALEXANDER DAHM. 4:4'-Dithiodiphenyl	i, 45
SCHMIDLIN (JULIUS) and MAXIMILIAN BERGMAN. The Autooxidation of Trinaphthylcarbinol	i, 46
GERHARDT (WALTER). Preparation of Acetal Condensation Derivatives from Polyhydroxy-alcohols with Aldehydes or Ketones	i, 47
MANELLI (EFISIO). Cubebin. IV. and V.	i, 47
MATHÉ (MICHAEL). Hydrolysis of <i>o</i> -Acetoxybenzoates and the Preparation of Calcium <i>o</i> -Acetoxybenzoate	i, 48
SCHÖTTE (JOH.) and PAVEL IV. PETRENKO-KRITSCHENKO. The Action of Hydrochloric Acid and Potassium Hydroxide on the Lactam of Benzoyldehydracetic Acid	i, 48
KLEMENC (ALFONSO). Nitrogenistic Acids	i, 49
BADISCHE ANILIN- & SODA-FABRIK. Preparation of Anthraquinone-carboxylic Acids	i, 49
MUMM (OTTO). Benzalacetoneoxalic Acid [Benzylidenacetetylvinic Acid]	i, 50
MATTINGER (FERDINAND). The Combination of Phenol-carboxylic Acids	i, 50
SCHMIDLIN (JULIUS) and ANTONIO GARCIA-BANCS. Isomeric and Tautomeric Organo-magnesium Compounds	i, 50
KAILAN (ANTON). The Action of Ultra-violet Light on <i>o</i> -, <i>m</i> -, and <i>p</i> -Nitrobenzaldehyde and on Benzaldehyde	i, 51
BAUDISCH (OSKAR). New Synthesis of <i>o</i> -Aldehydophenylnitrosylhydroxylamine	i, 52
SEIDA (HERMANN). Chemical Action of Light. II. Photo-Oxidation of the Aldehyde Group. I. Terephthalaldehyde	i, 52
SKITA (ALADAR) and W. A. MEYER. Catalytic Reduction. VII. The Preparation and Application of Colloidal Platinum Metals	i, 53
SKITA (ALADAR) and W. A. MEYER. Catalytic Reduction. VIII. Hydrogenation of Aldehydes and Ketones, and of Aromatic and Heterocyclic Substances in Colloidal Solutions	i, 54
WALLACH (OTTO) and W. VON RECHENBERG. Condensation Products of Cyclic Ketones with Acetone	i, 54
MONTAGNE (PIETER J.) and JACOB MOLL VAN CHARANTE. Action of an Alcoholic Solution of Potassium Hydroxide on Ketones. II.	i, 55
VORGÄNDER (DANIEL) and G. A. MEYER. Conversion of Distyryl Ketone into 2:6-Diphenylpyrone	i, 56
SCHOLL (ROLAND) and CHRISTIAN SEER [with OTTO VON SEYBELL]. Elimination of Hydrogen and Aromatic Nuclei and Union of the Latter by means of Aluminium Chloride	i, 56
BARGELIANT (GILBO) and MINA FINKELSTEIN. Chalkones and Hydrochalkones. II.	i, 59
CRSARIS (MARCELLO). Phenylhydroxyketoperinaphthimides	i, 60
BADISCHE ANILIN- & SODA-FABRIK. Preparation of <i>o</i> -Chloroanthraquinone	i, 61
BADISCHE ANILIN- & SODA-FABRIK. Preparation of Condensation Products of the Anthracene Series Containing Sulphur	i, 61
FABERFABRIKEN VOEM. FRIEDR. BAYER & CO. Preparation of Anthracene Derivatives	i, 61

	PAGE
MEYER (HANS), RICHARD BONDY, and ALFRED ECKERT. Binuclear Quinones of the Anthraquinone Group	i, 62
FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. Preparation of Borneol and 120 Borneol Esters	i, 63
RIEDEL (J. D.A.) Preparation of Odourless or Faintly Odourless Esters from Valeric Acid and Therapeutically Powerful Alcohols	i, 63
WALLACH (OTTO), RUD. MÜLLER, and FR. HENJES. Δ^4 -Menthen-3-one	i, 63
SKITA (ALADAR) [with JULIUS VON BERGEN, W. A. MEYER, and FRIEDRICH NORD]. Hydrogenation with Platinum Metals as Catalyst. VI. HÄMÄLÄINEN (JURO). [Glyconic Acids Produced by the Coupling of Alicyclic Compounds in the Organism]	i, 63
IPATIEV (VLADIMIR N.) [with N. MATOV and O. ROUTALAI]. The Simultaneous Action of Catalysts	i, 64
SEMMLER (FRIEDRICH W.) and FELIX RISSE. Constituents of Etheral Oils. The Sesquiterpene Selinene and its Derivatives	i, 65
GRAFE (VIKTOR). Extraction of Coffee Oil	i, 66
ALEXANDER (PAUL). Desulphuration of Vulcanised Rubber	i, 66
REUTTER (L.). Resin of <i>Pinus Halepensis</i>	i, 67
REUTTER (L.). The Resinous Exudation of <i>Pinus Peuce</i>	i, 67
MASSON (GEORGES). Chemical Composition of Dulcamara	i, 68
ANGELICO (FRANCESCO). Picrotoxin	i, 69
HOERMANN (PAUL). Picrotinic Acids	i, 70
FEIST (KARL). Tannin	i, 70
DOURIS (ROGER) and A. WIRTH. Action of Nitric Acid and Silver Nitrate on Tannin	i, 70
GOLDSCHMIEDT (GRIDO). Ratanhine	i, 71
FISCHER (HANS) and HEINRICH ROSE. Degradation of Bilirubin and Bilirubin Acid	i, 71
FISCHER (HANS) and HEINRICH ROSE. Bile Pigments. IV.	i, 71
FOSSE (ROBERT). Transformation of an Alcohol into a Sulphide or a Peroxide by Hydrogen Sulphide or Hydrogen Peroxide	i, 72
GOMBERG (MOSES) and C. J. WEST. Triphenylmethyl. XXI. Quinocarbenium Salts of the Hydroxyxanthenols	i, 72
KEHRMANN (FRIEDRICH) and TH. E. SHILLER. The Benzins of the Xyloquinols	i, 77
KEHRMANN (FRIEDRICH) [with E. ACKER, M. GUNTHER, and J. KNOP]. Ethers and Esters of Phthalicins and Benzins of Orcinol	i, 77
LIEBIG (HANS VON). Fluorescein	i, 79
BADISCHE ANILIN- & SODA-FABRIK. Preparation of Xanthenes of the Anthraquinone Series	i, 83
FARBWERKE VORM. MEISTER, LUCIUS & BEUNING. Preparation of Condensation Products in the Anthracene Series	i, 83
FARBWERKE VORM. MEISTER, LUCIUS & BEUNING. Preparation of "7,7'-Diaminobithindigo"	i, 83
LEGER (EMILE) and FERDINAND ROQUES. Capilline, a New Alkaloid from <i>Jaborandi</i>	i, 83
STOCKMAN (RALPH). Active Principles of <i>Cela Estalis</i>	i, 84
VEREINIGTE CHININFABRIKEN ZIMMER & Co. Preparation of Esters of Hydroquinone	i, 85
VEREINIGTE CHININFABRIKEN ZIMMER & Co. Preparation of Esters of Hydrogenated Cinchona Alkaloids	i, 85
EISSLER (FRANZ). Physostigmine [Eserine]	i, 85
BECKEL (AUGUST). α -Lupanine	i, 86
MANNICH (CARL). Morphineglycoside	i, 86
SCHOLTZ (MAX). Alkaloids of Pareira Root	i, 87
DANKOWITZ (PIETER W.). Protopine and Cryptopine	i, 87
KNOLL & Co. Preparation of Acyl Derivatives of Theobromine	i, 89
MOUREU (CHARLES) and AMAND VALEUR. The Chemical Constitution of Sparteine	i, 89
CORRIEZ (LOUIS). Some New Sparteine Salts	i, 89

	PAGE
CORRIEZ (LOUIS). The Constitution of Sparteine. Periodide and Sparteine Perbromide	i, 90
CORRIEZ (LOUIS). New α -Methylsparteinium Salts	i, 90
ABDERHALDEN (EMIL) and ERICH WURM. Pyrrolidonecarboxylic Acid and Polypeptides Derived from It	i, 90
BARGELLINI (GUIDO) and E. MARTEGIANI. Chalkones and Hydrochalkones. III	i, 90
MADELUNG (WALTER). Preparation of 2-Indolecarboxylic Acid and 2:3-Dihydroxyquinoline from Oxal- α -toluidic Acid. Indole Syntheses. II.	i, 91
CHEMISCHE FABRIK AUF AKTIEN FORM. E. SCHERING. Preparation of Derivatives of 2-Phenylquinoline-4-carboxylic Acid and its Homologues	i, 92
CONE (LEE H.). Salts of Acridine, Pyridine, and Quinoline	i, 92
KEHMANN (FRIEDRICH) and ZD. MATUSINSKY. Acridine Derivatives. II. Analogue of <i>pro</i> -Safranone in the Acridine Series	i, 93
FISCHER (HANS) and FR. KROLLPEFFER. Action of Phthalic Anhydride on Some Pyrrole Derivatives	i, 93
KEHMANN (FRIEDRICH) and A. BEYER. The Methylation of Gallocyain, Pyrogallin, and Azurin	i, 94
FARBWERKE FORM. MEISTER, LUCIUS & BRÜNING. Preparation of Anthrapyridonecarboxylic Acids	i, 95
FARBENFABRIKEN FORM. FRIEDR. BAYER & CO. Preparation of Anthraquinone Derivatives	i, 95
SCHAARSCHEMIDT (ALFRED) and ALEX. STAHLSCHEMIDT. 1-Amino-2-methylanthraquinone- α -quinolines	i, 95
BADISCHE ANILIN- & SODA-FABRIK. The Purification and Separation of Anthraquinonecarbidones from By-products	i, 96
FARBWERKE FORM. MEISTER, LUCIUS & BRÜNING. [Preparation of 4:4'-Diamino-2:2'-dimethylphenylmethane]	i, 96
FARBENFABRIKEN FORM. FRIEDR. BAYER & CO. Preparation of Amino-benzoyl Derivatives of Aminobenzoyl 7-amino-1-naphthol-3-sulphonic Acid	i, 96
BIANCHI (G.) [with MANLIO RUCCHI]. Action of Hydroxylamine acid of Phenylhydrazine on Urethanobenzylacetylacetone and on Ethyl Urethanobenzylacetoacetate	i, 96
STOLLÉ (ROBERT) and K. KRAUCH. Benzoylation of Amidonitazole	i, 97
SCHESTAKOV (PETER J.). Constitution of the Compound from Benzoyl Chlorocarbamide and Alkali	i, 97
BOBERT (T. MARSTON) and HARRY LINN FISHER. Preparation and Properties of 5-Aminoquinoline-6-carboxylic Acid and Certain Related Compounds	i, 98
CASELLA (LEOPOLD) & CO. Preparation of Condensation Products from 1-Chloro-2:4-dinitrobenzene with the Leucocondophenols derived from Carbazole	i, 98
VONGERICHTEN (EDUARD) and W. HOMANN. Constitution of <i>is</i> -Quinoline Red. II	i, 99
ORNDORFF (WILLIAM R.) and E. H. NICHOLS. Octachloroindigotin and Some Derivatives of Tetrachloroanthranilic and Tetrachlorophthalic Acids	i, 99
BADISCHE ANILIN- & SODA-FABRIK. [Preparation of Halogenated Derivatives of Indigoid Compounds]	i, 100
FARBWERKE FORM. MEISTER, LUCIUS & BRÜNING. Preparation of Condensation Products from Indigotin, its Homologues or Halogen-substitution Products	i, 100
BÜLOW (CARL). Buchner's Patrazolinecarboxylic Acids	i, 101
MANNICH (CARL) and W. KRÜSCH. Condensation Product of Formaldehyde, Ammonia, and Antipyrine	i, 101
KVM (OTTO) and L. RATKE. Substituted α -Hydroxy- and α -Methylbenzimidazoles	i, 102

	PAGE
BISTREZYCKI (AUGUSTIN) and GEORG PUZEWORSKI. Constitution of Compounds from <i>o</i> -Diamines and α -Hydroxy-acids. Acetylation of Benzimidazoles	i, 103
MÖHLAU (RICHARD). The Constitution of Acetyl- β -anthraquinonylmethylpyrazolone	i, 104
SCHAARSCHMIDT (ALFRED). Preparation of Nitrogenous Condensation Products of the Anthraquinone Series	i, 104
FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. Preparation of Anthraquinone Derivatives containing Nitrogen	i, 105
FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING. [Preparation of Anthracene Derivatives]	i, 105
ULLMANN (FRITZ) and JOHANN GNAEDINGER. Indamines	i, 105
BOBERT (MARSTON T.) and HARRY LINN FISHER. Synthesis of 1:3:7-Naphthazotriazines: Derivatives of a New Heterocyclic System	i, 106
CHEMISCHE FABRIK GRIEßHEIM-ELEKTRON. [Preparation of Anthracene Derivatives]	i, 107
OSTROGOVICH (ADRIANO). Methyliminotriazine	i, 107
RINGER (WILHELM E.) and J. I. J. M. SCHMUTZER. Quadriurates	i, 108
FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. Preparation of Amino-benzoylamino-compounds	i, 108
ZUNZ (EDGARD). Separation of Proteoses by Ultra-filtration	i, 108
PAULI (WOLFGANG) and OSKAR FALK. Changes in the Physical Conditions of Colloids. XIV. The Hydration of Various Protein Compounds with Special Reference to the Action of Caffeine	i, 108
CERVELLO (CARLO) and CORRADO VAVVARO. The Oxidation Relations of Certain Heavy Metals in Combination with Protein, and Some Physico-chemical Properties of the Same. II.	i, 109
LEVENE (PHOEBUS A.) and F. J. BIRCHARD. The Kyrine Fraction obtained on Partial Hydrolysis of Proteins. I.	i, 109
MICHAELIS (LEONOR) and H. PROBSTEN. The Isoelectric Point of Casein	i, 109
MARCILEWSKI (LEON). Blood Pigment	i, 110
BURKER (KARL). Nomenclature of Derivatives of the Blood Pigment	i, 110
KÜSTER (WILLIAM). Methylation of Hemin. IV.	i, 110
ARNOLD (VINZENZ). Preparation of Hematoporphyrin from Carbon Monoxide Blood	i, 111
FISCHER (HANS) and FRIEDRICH MEYER-BETZ. Formation of Porphyrin	i, 111
BANG (IVAR). (Guanylic Acid)	i, 111
KLECKER (KG. O. AF.). The Pentose of Guanylic Acid	i, 111
PALITZSCH (SVEN) and L. E. WALBUM. The Optimal Hydrogen-ion Concentration for the Liquefaction of Gelatin by Trypsin	i, 112
CHRISTIANSEN (JOHANN). The Mechanism of Pepsin Digestion	i, 112
MELLANBY (JOHN) and V. J. WOOLLEY. The Enzymes of the Pancreas. I. The Generation of Trypsin from Trypsinogen by Enterokinase	i, 113
PANZER (THEODOR). Action of Hydrogen Chloride on Invertase. II.	i, 113
PANZER (THEODOR). Action of Hydrogen Chloride on Diastase. I.	i, 113
HEYL (RUTGER CISON). Malt Diastase, and the Action of Potassium Phosphates on it	i, 114
HEDIN (SVEN G.). Reaction between Enzymes and Other Substances	i, 114
JOHANSSON-BLOHM (G.). The Action of Certain Colloids on the Inhibition of Enzyme-actions	i, 114
MELLANBY (JOHN). The Coagulation of Milk by Rennet	i, 114
WOLFF (JULES). The Biochemical Role of Peroxy-lases in the Transformation of Orcinol into Orcin	i, 115
BATTIELLI (FR.) and (Mlle.) LINA STERN. The Nomenclature of the Polyphenoloxidas-s	i, 115
BART (HEINRICH). Preparation of Organic Arsenic Compounds	i, 115
FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING. Preparation of Derivatives of 3:3'-Diamino-4:4'-dihydroxyarsenobenzene	i, 116
FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING. Preparation of Unsymmetrical Aromatic Arsenic compounds	i, 116

CONTENTS

ix

	PAGE
FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING. Preparation of Products Reduced Beyond the Arsenic-stage from Substituted Aromatic Arsinic Acids	i, 117
TAFEL (JULIUS). Formation of Organo-metallic Compounds during Electrolytic Reductions	i, 117
FOURNEAU (ERNEST) and A. VILA. Chemo-therapeutical Researches on Mercury Compounds. Mercuridi- <i>p</i> -aminophenol	i, 117
FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. Preparation of Nuclear-substituted Mercury Derivatives of Polysubstituted Phenols	i, 118
VEREINIGTE CHEMISCHE WERKE AKTIENGESellschaft. Preparation of Derivatives of Aminobenzoic Acid and its Salts Containing Mercury in the Ring	i, 118
VEREINIGTE CHEMISCHE WERKE AKTIEN-Gesellschaft. Preparation of Dinitrodiphenylmercuridicarboxylic Acids	i, 118
SCHOELLER (WALTER) and WALTHER SCHRAUTH. Preparation of Esters of Aromatic Carboxylic Acids containing Mercury and their Products of Hydrolysis	i, 119

Physiological Chemistry.

HASSELBALCH (KARL A.). The Regulation of Neutrality by the Respiratory Centre, and its Stimulability in Maintaining the Carbon Dioxide Tension of the Blood	i, 119
BROTHBY (WALTER M.). Absence of Apnoea After Forced Breathing	i, 120
WIENER (HUGO). The Differences in Composition between Arterial and Venous Blood	i, 120
GERARD (P. J.). Distribution of Sodium and Potassium in the Animal Organism	i, 120
BACKMAN (E. LOUIS). The Influence of Nitrogenous Metabolism Products which Occur Naturally in Blood and Urine on the Blood Pressure	i, 120
ANKER (G. VON). The Part Played by the Suprarenals in the Normal Vascular Reactions of the Body	i, 121
ANKER (G. VON). Local Vascular Reactions and their Interpretation	i, 121
LOB (WALTHER) and S. GUTMANN. Glycolysis. III. The Influence of Glycine and Boric Acid Anions on the Oxidative Destruction of Dextrose in the Presence of Phosphates	i, 121
OHTA (KOHSHI). The Significance of Proteolysis in Specific Hemolysis	i, 121
MICHAELIS (LEONOR) and HEINRICH DAVIDSON. The Influence of the Hydrogen Ion Concentration on Specific Precipitin Reactions	i, 121
FELD (ERNST) and ERICH SCHLESINGER. The Coagulation of Blood	i, 121
HALDANE (J. B. S.). The Dissociation of Oxyhemoglobin in Human Blood During Partial Carbon Monoxide Poisoning	i, 122
ROBERTSON (T. BRATSFORD). Blood-relationships of Animals as Displayed in the Composition of the Serum-proteins. I. A Comparison of the Serum of the Horse, Rabbit, Rat, and Ox in the Normal and Fasting Condition	i, 122
HIRATA (GOICHI). The Diastatic Action of Human Saliva	i, 123
LÓPEZ-SUÁREZ (J.). Formation of Hydrochloric Acid in the Stomach	i, 123
DAVIDSON (HEINRICH). The Fat-hydrolysing Ferment in Gastric Juice, and its Estimation	i, 123
WHITE (GEORGE F.) and ADRIAN THOMAS. Tryptic Digestion of <i>Cynoscion regalis</i>	i, 123
LESK (GRAHAM) and J. H. RICHE. Animal Calorimetry. V. The Influence of the Ingestion of Amino-acids on Metabolism	i, 123
LESK (GRAHAM) and J. A. RICHE. Animal Calorimetry. VI. The Influence of Mixtures of Food-stuffs on Metabolism	i, 124
MOTTHAM (V. H.). Fatty Acid Metabolism in the Liver. II. The Relation of the Fatty Acids in the Food of the Mouse to those in their Livers and Myotomes	i, 124

	PAGE
SMEDLEY (MISS IDA). The Biochemical Synthesis of Fatty Acids from Carbohydrates	i, 124
OSBORNE (THOMAS B.), LAFAYETTE B. MENDEL, and EDNA L. FERRY. Maintenance Experiments with Isolated Proteins	i, 124
PATTA (ALDO). The Influence of Lecithin on the Nitrogen and Phosphorus Balance	i, 125
GRAFE (E.). Retention of Nitrogen after Feeding on Ammonium Salts	i, 125
McCOLLUM (ELMER V.) and H. STRENSOCK. The Creatine Metabolism of the Guinea Pig	i, 125
LEWIS (HOWARD B.). The Behaviour of Some Hydantoin Derivatives in Metabolism. I. Hydantoin and Ethyl Hydantoate	i, 125
SCAFFIDI (VITTORIO). Purine Metabolism. X. The property of the Organism to Destroy, or Form by Oxidative Processes, Uric Acid in Animals Capable of Producing this Acid Synthetically	i, 126
HUNTER (ANDREW) and MAURICE H. GIVENS. The Metabolism of Endogenous and Exogenous Purines in the Monkey	i, 126
FOLIN (OTTO) and HARRY LYMAN. Absorption from the Stomach	i, 126
MARCONDA (PAOLO). Behaviour of Intestinal Wall After a Prolonged Period of Functional Inactivity	i, 126
JANSEN (BARREND C. P.). Absorption of Cholic Acid in the Dog's Intestine	i, 126
RONA (PETER). The Fate of Deeply-degraded Proteins in the Intestine	i, 127
LOEB (JACQUES). The Investigation of the Permeability and Antagonistic Action of Electrolytes by means of a New Method	i, 127
STARKENSTEIN (EMIL). The Influence of Neutral Salts on Ferment Action. II	i, 128
FRÄNKEL (STEGMUND), P. KIRSCHBAUM, and KURT LINNERT. Lipoids. XVI. The Cholesterol Content of Different Parts of the Brain	i, 128
MAKINESCO (G.). The Colloidal Structure of Nerve Cells and the Changes which they Undergo	i, 128
CARBONE (DOMENICO) and GIACOMO FIGHINI. Chemical and Biochemical Investigations on the Nervous System under Normal and Pathological Conditions. IV. The Chemical Composition of the Brain in Progressive Paralysis	i, 128
DIXON (WALTER E.) and FRED RANSOM. Broncho-dilator Nerves	i, 129
BURRIDGE (W.). The Influence of Inorganic Salts on the Perfused Heart	i, 129
LOEWI (OTTO). Physiology and Pharmacology of the Cardiac Vagus. I. The Influence of Chloral Hydrate on the Result of Vagus Stimulation	i, 129
LOEWI (OTTO). Physiology and Pathology of the Cardiac Vagus. II. The Importance of Calcium for Vagus Action	i, 129
LOEWI (OTTO). Physiology and Pharmacology of the Cardiac Vagus. III. Vagus Excitability and Vagus Poisons	i, 130
LOEB (ADAM). The Behaviour of Acetic Acid in the Artificial Perfusion of the Liver	i, 130
HAAS (GEORGE). The Fate of Glyoxylic Acid in the Animal Body	i, 130
CLARK (A. J.). The Destruction of Alkaloids by the Body Tissues	i, 130
BOSTOCK (GRETRUDE D.). The Distribution of Nitrogen in Autolysis, with Special Reference to Deaminisations	i, 131
KONSCHEGG (ARTHUR VON). The Permeability of the Kidneys to Sugar after Repeated Injections of Adrenaline	i, 131
SCHULZ (HEGO). The Amount of Silicic Acid in Human Thyroid Glands	i, 131
ROWE (ALBERT HOLMES). The Creatine-splitting Enzyme of the Parathyroids and the Suprarenals	i, 132
MOHR (L.) and W. HEIMANN. The Chemistry of Normal and Eclamptic Placenta	i, 132
BERG (WILLIAM N.). The Physico-chemical Basis of a Theory of Muscular Contraction (Zuntz's Theory)	i, 132
DALE (HENRY H.). The Anaphylactic Reaction of Pain Muscle in the Guinea Pig	i, 132
McCOLLUM (ELMER V.), J. G. HALPIN, and A. H. DEESCHER. Synthesis of Lecithin in the Hen and the Character of the Lecithins Produced	i, 132

	PAGE
GRANDMOUGIN (EUGÈNE). Red Colouring Matter of Boiled Crabs . . .	i, 132
SCHÜBEL (KONRAD). The Bio-chemistry of Termites. The Chemical Composition of the Faecal Stalactites of <i>Entermes monoceros</i> . . .	i, 133
DENIS (W.). Metabolism Studies on the Cold-blooded Animals. I. The Urine of the Fish . . .	i, 133
HAMÄLÄINEN (JUHO). Behaviour of Alicyclic Compounds in Coupling with Glyconic Acid in the Organism . . .	i, 133
FREUND (ERNST) and GISA KAMINER. The Relationships between Tumour Cells and Blood-serum . . .	i, 135
BELL (E. T.). The Interstitial Granules (Liposomes) in Fatty Metamorphosis of Striated Muscle . . .	i, 135
KLAUSNER (G.). Nature of the So-called Klausner Serum Reaction . . .	i, 135
CATHCART (E. PROVAN) and J. HENDERSON. Bence-Jones Proteinuria . . .	i, 136
ITAMI (S.). The Action of Carbon Dioxide on the Vascular System . . .	i, 136
FERRON (D.). Diuretic Action of Mercury Preparations . . .	i, 136
KOLLE (WILHELM), M. ROTHERMUND, and S. PESCHLE. Action of Mercury Preparations on Spirochaete Diseases. I. Chemical-therapeutic Action of Mercury Compounds, Especially of a New Mercury Preparation which Strongly Attacks Spirochaete, but is only very slightly Poisonous . . .	i, 136
ARELIN (L.). Action of Mercury Preparations on Spirochaete Diseases. II. The Toxicology and Pharmacology of Some Mercury Compounds . . .	i, 136
GRAMENITZKI (M. J.). The Sugar of the Blood and Urine under the Influence of Continuous Adrenaline Infusion . . .	i, 137
TRIBE (E. M.). Effect of Adrenaline on the Pulmonary Circulation . . .	i, 137
BERTON-OPITZ (RUSSELL). The Vascularity of the Liver. VIII. The Influence of Adrenaline on the Arterial Inflow . . .	i, 138
BERTON-OPITZ (RUSSELL). The Vascularity of the Liver. IX. Influence of Amyl Nitrite on the Arterial Inflow . . .	i, 138
BERTON-OPITZ (RUSSELL). The Vascularity of the Liver. X. The Influence of Adrenaline on the Venous Inflow . . .	i, 138
SKÓRCZEWSKI (WITOLD) and J. SOHN. Metabolism Experiments in the Administration of Atophan . . .	i, 138
SKÓRCZEWSKI (WITOLD). Why Does Atophan Increase the Excretion of Uric Acid? . . .	i, 138
SIEGFRIED (MAX) and R. ZIMMERMANN. The Formation of Phenol from <i>p</i> -Cresol in the Organism of the Dog . . .	i, 139
EPSTEIN (ALBERT A.) and SAMUEL BOOKMAN. Formation of Glycine in the Body. II.	i, 139
DIXON (WALTER E.) and W. E. LEE. Tolerance to Nicotine . . .	i, 139
BATTIELLI (FR.) and (Mlle.) LINA STEEN. The Oxidation of <i>p</i> -Phenylenediamine by Animal Tissues . . .	i, 140
BATTIELLI (FR.) and (Mlle.) LINA STEEN. The Influence of Various Factors on the Oxidation of <i>p</i> -Phenylenediamine by Animal Tissues . . .	i, 140
CHISTONI (ALFREDO). Pharmacology of Picrotoxin, Picrotin, and Picrotoxinin . . .	i, 140
LANGGAARD (ALEXANDER). The Poisonous Nature of Methyl and Ethyl Alcohols . . .	i, 141
DELZENNE (C.) and Mlle. S. LEDER. Haemolytic Substances Obtained from Serum, and the Vitellus of Eggs Submitted to the Action of Venoms . . .	i, 141

Chemistry of Vegetable Physiology and Agriculture.

TSCHACHOFF (SERGEI). A Hygienic Pipette for Bacteriological and Chemical Work . . .	i, 142
VIERHOEYER (A.). Detection of Chitin in Bacteria . . .	i, 142

	PAGE
KEYES (FREDERICK G.) and LOUIS J. GILLESPIE. Gas Metabolism of Bacteria. I. Fermentation of Dextrose by <i>Bacillus coli</i> , <i>B. typhosus</i> , and <i>Bacterium welchii</i>	5, 142
KEYES (FREDERICK G.) and LOUIS J. GILLESPIE. Gas Metabolism of Bacteria. II. The Absorption of Oxygen by Growing Cultures of <i>Bacillus coli</i> and <i>Bacterium welchii</i>	5, 142
AGULHON (HENRI) and R. SAZERAC. Activation of Certain Processes of Microbic Oxidation by Uranium Salts	5, 143
TRILLAT (AUGUSTE) and M. FOUCASSIER. Action of Infinitesimal Doses of Different Alkaline Substances, Fixed or Volatile, on the Vitality of Microbes	5, 143
REITGER (LEO F.) and CLYDE R. NEWELL. Putrefaction with Special Reference to the <i>Proteus</i> Group	5, 143
JOHANNESSEN (FRITZ). The Influence of Organic Acids on the Fermentation by Yeast	5, 143
LEBEDEV (ALEXANDER VON). The Mechanism of Alcoholic Fermentation	5, 144
LEBEDEV (ALEXANDER VON) and N. GRIAZNOV. The Mechanism of Alcoholic Fermentation. II.	5, 144
LINDER (LEON) and L. AMMANN. Influence of Pressure on Alcoholic Fermentation	5, 144
NEUBERG (CARL) and JOHANNES KERR. Is Ethyl Alcohol Produced by Yeast Fermentation in Absence of Sugar?	5, 145
EULER (HANS VON) and TH. BERGGREN. The Primary Transformation of Hexoses by Alcoholic Fermentation	5, 145
IVANOV (NICOLAUS). The Effect of Phosphates on the Work of the Proteolytic Enzymes in Yeast	5, 145
SAUTON (BENJAMIN). Comparative Influence of Potassium, Rubidium, and Cesium on the Development and Sporulation of <i>Aspergillus niger</i>	5, 146
DOX (ARTHUR W.) and RAY E. NEIDIG. The Scission of α - and β -Methylglucoside by <i>Aspergillus niger</i>	5, 146
JEGOROV (M. A.). The Behaviour of Moulds (<i>Aspergillus niger</i> and <i>Penicillium crustaceum</i>) towards Phytin	5, 146
KOSSOWITZ (ALEXANDER). Decomposition of Carbamide, Uric Acid, Hippuric Acid, and Glycine by Moulds	5, 146
MEYERHOF (OTTO). The Apparent Respiration of Dead Cells in the Reduction of Pigments	5, 146
ACQUA (C.). The Action of Uranium on the Plant Cell	5, 147
KUSTER (E.). Absorption of Aniline Dyes in Living Plant Cells	5, 147
BRUTNER (REINHARD). The Physical Character of Bio-electrical Differences of Potential	5, 147
SCHULOV (IVAN). Sterile Cultures of a Higher Plant. Assimilation of Nitrogen as Ammonia and as Nitrates	5, 147
WEKVERS (TH.). Localisation and Function of Potassium in Plants	5, 147
GORTER (K.). Chlorogenic and Saccharic Acids in Latex	5, 148
ZALESKI (W.) and ELISABETH MARX. The Carboxylase of Higher Plants	5, 148
BUSCHMANN (E.). Basic Constituents of Fly Azaric	5, 148
GRAFE (VIKTOR) and V. VOJK. The Inulin Metabolism of <i>Cichorium Jaculus</i> (Chicory). II. The Formation and Storage of Inulin	5, 148
ANDERSON (R. J.). The Organic Phosphoric Acid of Cottonseed Meal	5, 149
KYLIN (HARALD). Pigments of the <i>Escalier</i>	5, 149
BRIDEL (MARCE). Presence of Gentiopicroin, Gentianose, and Sucrose in the Fresh Roots of <i>Gentiana Asch-podenii</i>	5, 149
OESTERLE (OTTO A.). The Constituents of Ipe-tobacco Wood (<i>Bignonia toecaria</i>)	5, 149
KORSAROV (MILÉ. MARIE). Variations of the Fatty Matters, Sugars, and Saponin during the Maturation of Seeds of <i>Lycium chilense</i>	5, 149
BRIDEL (MARCE). Presence of Gentiopicroin in <i>Sarcocolla peruviana</i>	5, 150
LITTMANN (EDMUND O. VON). Occurrence of Trehalose, Vanillin, and d -Sorbitol	5, 150
MAXIMOV (N. A.). Chemical Means of Protecting Plants from Frost	5, 150

CONTENTS.

xiii

	PAGE
JACOBSON (C. A.). Alfalfa. IV. Enzymes Present in Alfalfa Seeds . . .	i, 151
HART (EDWIN B.), GEORGE C. HUMPHREY, and F. B. MORRISON. Comparative Efficiency for Growth of the Total Nitrogen from Alfalfa Grass and Corn Grain . . .	i, 151
ALYISI (UGO). Observations on the Action of Fluorine in Nature . . .	i, 151
PELLLET (HENRI). Reducing Substances Present in Fresh Sugar Beets. Their Influence on the Direct Estimation of Sucrose in the Beet . . .	i, 151
GRÉGOIRE (ACH.) and EM. CARRIAUX. Sesame Cake . . .	i, 152
GIL (G.). The Black Earths of the Valley of Foned R'Don in Morocco . . .	i, 152
NOTTIN (P.). Agronomic Study of Manganese . . .	i, 152
MILO (C. J.). Nitrolin and its Decomposition in the Soil. III. . .	i, 152

PART II.

General and Physical Chemistry.

LIESE (ERNST). The Band Spectrum of Mercury . . .	ii, 1
GRAFFDYK (Mlle. I. M.). Magnetic Resolution of the Spectra of Nickel, Cobalt, and Iron . . .	ii, 1
PASCHEN (FRIEDRICH) and E. BACK. Normal and Anomalous Zeeman Effects . . .	ii, 2
PURILLIAN (NILS). A New Proof of the Existence of Molecules. V. . .	ii, 2
SPARK (JOHANNES). Relationship between Fluorescence and Chemical Constitution . . .	ii, 2
TCHUGAIEV (LEO A.). A New Method for Examining Optically Active Compounds: Anomalous Dispersion . . .	ii, 3
WEIGERT (FRITZ). The [Chemical] Efficiency of Light Energy . . .	ii, 3
ODOLNSKY (W.). Photo-electric Action of the Extreme Ultra-violet on Water, Aqueous Solutions, and Ice . . .	ii, 3
WILLOWS (R. S.). Photo-electric Effect of Some Compounds . . .	ii, 4
BERRY (HENRI, VICTOR HENRI, and ALBERT RANC). Inversion of Sucrose by Ultra-violet Rays . . .	ii, 4
BERTHELOT (DANIEL) and HENRI GAUDERON. Photolysis of Different Classes of Sugars by Ultra-violet Light . . .	ii, 4
SODDY (FREDERICK). Secondary γ -Rays Excited by the β -Rays of Radium . . .	ii, 4
RUTHERFORD (ERNEST). The Energy of the Groups of β -Rays from Radium . . .	ii, 4
LUNKENHEIMER (FRITZ). The Ratio of the Intensities of the Hydrogen Canal Ray Lines . . .	ii, 5
GEHRCKE (ERNST) and R. SEELIGER. Luminosity of Gases under the Influence of Cathode Rays. II. . .	ii, 5
PEDDER (GORDON S.). Spectra of Low Potential Discharges in Air and Hydrogen . . .	ii, 5
VOLMER (M.). The Emission of Negative Corpuscles by Certain Salts which have Previously been Subjected to Cathode Rays . . .	ii, 6
DRANE (WILLIAM). Effect Produced by a Magnetic Field on Ionisation Currents . . .	ii, 7
KAILAN (ANTON). The Chemical Action of Penetrating Radium Rays. III. The Influence of the Penetrating Rays on Some Inorganic Compounds . . .	ii, 7
KAILAN (ANTON). The Chemical Action of Penetrating Radium Rays. IV. The Influence of the Penetrating Rays on Some Organic Compounds and Reactions . . .	ii, 8
BROWN (F. C.). Evidence that Sodium belongs to a Radioactive Series of Elements . . .	ii, 8
LABORDE (A.) and ABOLPHE LEPAGE. Radioactivity of the Springs at Vichy and Other Places . . .	ii, 9

	PAGE
BÖCK (F.) and LUDWIG MOSER. The Action of the Silent Electric Discharge on a Mixture of Hydrogen and Titanium Tetrachloride. I.	ii, 9
GERLHOFF (GEORG). The Glow Discharge in Very Pure Gases	ii, 9
BOUTY (EDMOND). An Attempt to Determine the Dielectric Cohesion of a Rare Gas, with Small Quantities of Material	ii, 10
SCHLEICHER (A. P.). Electrical Resistance Measurements of Mixtures of Copper and Mercury	ii, 10
LEDoux (R.). Electrical Conductivity of Copper-Tin Alloys (a Correction)	ii, 10
HAIRSTO (G. E.). Variation of the Conductivity of Aluminium Anode Films with Temperature	ii, 10
MÜLLER (JOSEPH A.). Relative Electrical Conductivity and Ionisation of Aqueous Solutions of Hydrogen Chloride between 18° and 81°	ii, 11
HOWARD (S. F.) and HARRY C. JONES. Conductivity, Temperature-coefficients of Conductivity, and Dissociation of Certain Electrolytes in Aqueous Solution at 35°, 50°, and 65°	ii, 11
FITZGERALD (FRED. F.). The Electrical Conductivity of Solutions in Methylamine and Ethylamine; The Fluidity of Ammonia, Methylamine and Sulphur Dioxide, and the Fluidity of Certain Solutions in these Solvents	ii, 12
ROSHDESTWENSKY (ALEXANDER P.) and WILLIAM C. McC. LEWIS. Electrocapillary Pulsation of a Mercury Meniscus	ii, 13
OOSTERHUIS (E.). The Peltier Effect and the Iron-Mercury Thermo-electric Couple	ii, 13
HEYEST (GEORG VON) and ROLAND E. SLADE. Electro-chemical Behaviour of Tantalum	ii, 13
BAUR (EMIL) and H. EHRENBERG. New Fuel Batteries	ii, 13
DEVENTER (CHARLES M. VAN). Self-induction in Concentration Cells	ii, 14
CUMMING (ALEXANDER C.). The Elimination of Potential due to Liquid Contact. II. A Simple Equation for the Calculation of the Diffusion Potential	ii, 14
THIEL (ALFRED) and E. BREUNING. New Experiments on the Super-tension of Hydrogen	ii, 15
KREMANX (ROBERT) and R. SCHOLZ. The Polyiodides. II. Periodic Phenomena in the Electrolysis of Solutions of the Alkali Iodides	ii, 15
BAGSTER (LANCLOT S.) and BERTRAM D. STREEL. Electrolysis in Liquefied Sulphur Dioxide	ii, 15
DUPUY (EUGÈNE L.) and A. PORTEVIN. The Thermo-electric Properties of the System Iron-Nickel-Carbon	ii, 16
SLADE (ROLAND E.). Electric Furnace for Experiments in a Vacuum at Temperatures up to 1500°	ii, 16
ALIERTHUM (HANS). The Hall Effect in Metals at Low Temperatures and the Theory of Magnetism from the Point of View of the Theory of Quanta	ii, 16
WEISS (PIERRE) and AUGUSTE PICARD. Magnetisation of Water and Oxygen	ii, 17
HADFIELD (SIR ROBERT), EDWARD COLVER-GLAUCERT, SIEGFRIED HILPERT, PIERRE WEISS, H. KAMERLINGH ONNES, EDGAR WEDERIND, FRIEDRICH HEPSLER, E. TAKE, ALEXANDER D. ROSS, and THEODOR DIECKMANN. The Magnetic Properties of Alloys	ii, 17
GUMBLICH (ERICH) and PAUL GÖRGENS. Magnetic Properties of Iron-Carbon and Iron-Silicon Alloys	ii, 17
GRAY (JAMES G.) and ALEXANDER D. ROSS. The Magnetic Properties of Special Steels at Low Temperatures	ii, 18
KNOWLTON (A. A.) and O. C. CLIFFORD. The Hensler Alloys	ii, 18
WEBER (RUDOLF H.). Magnetic Susceptibility of Ferric Salts	ii, 18
DUCLOUX (JACQUES). Specific Heat of Substances at Low Temperatures	ii, 18
SLADE (ROLAND E.) and F. D. FAIRROW. The Dissociation Pressure and Melting Points of the System Copper-Cuprous Oxide	ii, 18
BECKMANN (ERNEST). Cryoscopic Determinations in Iodine	ii, 19
MAMELI (ELISAB.) and ANNA MASSERRIER. Polymorphism	ii, 19

	PAGE
RAUD (ÉMILE). Cryoscopic Researches	ii, 19
JOUNIAUX. Thermal Constants of Camphor	ii, 20
BECKMANN (ERNST). Ebullioscopy of Iodine	ii, 20
PERMAN (EDGAR P.) and TUDOR W. PRICE. Vapour-pressure of Concentrated Aqueous Solutions	ii, 20
CHOMMELIN (C. A.). Triple Point of Methane	ii, 20
BOUTARIC (A.). The Critical Coefficient and the Molecular Weight of Substances at the Critical Point	ii, 21
BRINER (ÉMIL). The Limit of Formation of Endothermic Compounds at Very High Temperatures	ii, 21
BJERRUM (NIELS). The Behaviour of Iodine and Sulphur at Extremely High Temperatures, from Explosion Experiments	ii, 21
SWARTS (FRÉDÉRIC). Heat of Formation of Some Organic Fluorine Compounds. IV.	ii, 22
KOLOSOVSKI (NICOLAS). Thermochemical Researches on Solution	ii, 22
WEBERLT (ARTHUR) and CHR. MUSCELEANU. Heat of Vaporisation of the Metals	ii, 23
LEWIS (GILBERT N.) and GEORGE H. BURNHOLS. Free Energy of Organic Compounds. I. Reversible Synthesis of Carbamide and of Ammonium Cyanate	ii, 23
MERNIER (JEAN). New Forms of Whirling Gaseous Combustion and Their Analogy with the Appearance of Certain Astronomical Phenomena	ii, 24
GARVER (MADISON M.). Polymerisation of Liquids and a General Method for Determining its Relative Value	ii, 24
GARVER (MADISON M.). A Thermodynamic Measure of Polymerisation	ii, 25
KEESON (W. H.). The Second Virial Coefficient for Monatomic Gases and for Hydrogen Below the Boyle Point	ii, 25
HEIZ (WALTER) and W. RATHMANN. Physical Constants of Certain Important Chlorinated Hydrocarbons Used as Solvents	ii, 26
HANRIOT (MAURICE). The Drawing Out of Metals	ii, 26
BATSCHINSKI (ALEXIS J.). Viscosity Law for Liquids	ii, 26
KLEEMAN (RICHARD D.). Effect of the Transition Layer of a Liquid on its Surface Tension	ii, 26
KATZ (J. R.). The Laws of Surface Adsorption and the Potential of Molecular Attraction	ii, 27
ROHLAND (PAUL). Adsorption by Clays. IV.	ii, 27
FRIEDRICH (K.). Thermal Dissociation and Constitution of Readily Decomposable Salts	ii, 27
FRIEDRICH (K.) and L. GARRETT SMITH. Thermal Dissociation and Constitution of Readily Decomposable Minerals	ii, 28
GILLET (ALF.). Mechanism of Osmosis	ii, 28
SIERN (OTTO). The Kinetic Theory of the Osmotic Pressure of Concentrated Solutions, and the Agreement of Henry's Law for Concentrated Solutions of Carbon Dioxide in Organic Solvents at Low Temperatures	ii, 28
LEWIS (GILBERT N.). Activity of the Ions and the Degree of Dissociation of Strong Electrolytes	ii, 29
ESKELAR (JOHANNES E.). Neutralisation Curves and Dissociation Constants of Sulphuric and Citric Acids	ii, 29
MÜLLER (CARL). The Absorption of Oxygen, Nitrogen, and Hydrogen in Aqueous Solutions of Non-electrolytes	ii, 30
DENISON (ROBERT B.). Liquid Mixtures. I. Property-composition Curves and the Molecular Changes which take Place on Forming Binary Liquid Mixtures	ii, 30
DENISON (ROBERT B.). Liquid Mixtures. II. Chemical Combination in Liquid Binary Mixtures as Determined by a Study of Property-composition Curves	ii, 30
WEIMANN (P. P. VON). Systematics of the States of Aggregation of Matter	ii, 31
KRILIOV (BASIL). The Nature of Pseudo-solutions	ii, 31

	PAGE
MICHAELIS (LEONOR). The Theory of the Isoelectric Point. III. The Nature of Solutions of Colloids of the Character of Proteins	ii, 31
WEIMARN (P. P. VON). Theory of the Formation and Stability of Colloidal Solutions and Precipitates. II.	ii, 31
PHILIPPSON (MAURICE). Formation of New Colloids in a Colloidal Solution by Metallic Plates	ii, 32
OSTWALD (WOLFGANG). The Emulsoid Condition and the General Classification of Colloidal Forms	ii, 32
WEIMARN (P. P. VON). Jellies	ii, 32
SCHAEFFER (F. E. C.). Maximum and Minimum Equilibrium Pressure in Binary Systems	ii, 32
HERZ (WALTER) and FRITZ KUNTZE. Examples of Bimolecular Reversible Reactions	ii, 33
NIGGLI (PAUL). Gaseous Mineralisers in a Magma. II.	ii, 33
PARRAYANO (NICOLA). Equilibria in Quaternary Systems. V. Completely Isomorphous Quaternary Mixtures	ii, 33
REINDERS (WILLEM) and D. LELY, jun. Distribution of Dyes between Two Solvents. The Theory of Dyeing	ii, 33
GOEBEL (J. B.). The Calculation of Equilibrium Constants from Cryoscopic Measurements	ii, 34
MENGE (OTTO). [Reciprocal Salt Pairs]	ii, 34
BOULANGER (CH.) and GEORGES URDAIN. Theory of the Efflorescence of Saline Hydrates	ii, 34
MÜLLER (JOSEPH A.). Saturation of the Ethylenic Bands of Oleic Acid by means of Iodine and the Molecular Weight of Dissolved Iodine	ii, 34
LINHART (GEORGE AL). Hydrolysis of Metallic Alkyl Sulphates	ii, 35
SMITH (L.). The Alkaline Decomposition of Chlorohydrins	ii, 35
BLACKADDER (THOMAS). Inorganic Ferments. VI. Catalytic Decomposition of Formic Acid by Rhodium	ii, 36
STIEGLITZ (JULIUS). Catalysis on the Basis of Work with the Imino-esters: the "Salt Effect"	ii, 36
KLEINER (A.). The Natural System of the Elements	ii, 37
RADULESCU (DAN). The Theory of Radicles as an Interpretation of Mendeleev's System	ii, 37
BELLUCCI (ITALO). Some Considerations Regarding Werner's Theory	ii, 38
BERLIN (ERNST). Laboratory Apparatus	ii, 38
FICHTER (FRITZ). Lecture Experiment on the explosion [and Production] of Electrolytic Gas by Alternating Currents	ii, 38
BAUDISCH (OSKAR) and ROSE FÜRST. Photochemistry. IV. Photochemical Lecture Experiments	ii, 38

Inorganic Chemistry.

BRIDGMAN (P. W.). The Behaviour of Water as a Liquid and in Five Solid Modifications Under Pressure	ii, 39
ATEN (A. H. W.). A New Modification of Sulphur	ii, 40
LEFEBVRE (H. L. DE). The Relation between the Sulphur Modifications	ii, 40
MORGAN (WILLIAM C.). Alleged Complexity of Tellurium	ii, 41
JAEGER (FRANK M.) and J. B. MENKE. [Compounds of Tellurium and Iodine]	ii, 41
MENKE (J. B.). The Ternary System Tellurium Tetra-iodide-Hydrogen Iodide-Iodine, and the Estimation of Tellurium by means of Hydrazine Hydrate	ii, 41
PETERS (WALTER). The Validity of Werner's Theory of Subsidiary Valencies for Ammoniates	ii, 42
BAXTER (GREGORY P.) and CHARLES J. MOORE. Revision of the Atomic Weight of Phosphorus. III. Analysis of Phosphorus Trichloride	ii, 43
STOCK (ALFRED), GEORGE E. GIBSON, and ERICH STAMM. The Density of Phosphorus Vapour	ii, 43

	PAGE
STOCK (ALFRED) and CARL MASSENEZ. Boron Hydrides	ii, 44
TAMMANN (GUSTAV). Condition Diagram of Carbon Dioxide	ii, 45
STOCK (ALFRED) and PAUL PRAETORIUS. Carbon Subsulphide, C_2S_2	ii, 46
WARTENBERG (H. VON). The Reduction of Silica	ii, 47
KITTL (ERWIN). The Velocity of Crystallisation and Crystallising Power of Silicates	ii, 47
MEYER (FRIEDRICH) and ARTHUR STÄHLER. The Proportion of Potassium Chloride in Potassium Chlorate, and the Nephelometric Control	ii, 48
ARNDT (KURT) and HEINRICH HUGO KUNZE. Molten Carnallite	ii, 49
MENEGHINI (D.). Thermal Analysis of Binary Mixtures of Alkali Nitrites with Other Salts of the Same Metals	ii, 49
TRAUBE (WILHELM). The Action of Ozone on Alkali Hydroxides	ii, 49
PRAUSNITZ (PAUL. H.). The Electrolytic Preparation of Sodium Hypochlorite	ii, 49
BRÜHL (Mlle. H.). Crystallographic Study of Lithium Chlorate	ii, 50
BALLG (REZSO) and EMIL DITTLER. The Binary System $Li_2SiO_3 - Al_2(SiO_3)_2$	ii, 51
TILLMANN (J.) and O. HEUBLEIN. The Carbonic Acid of Natural Waters which is Able to Attack Calcium Carbonate	ii, 51
OCHSNER DE CONINCK (WILLIAM). Physical Action of Neutral Reagents on the Tribasic Alkaline Earth Phosphates. Investigation of the Colloidal State	ii, 51
BRUSTI (GIUSEPPE) and CARLO SANDONNINI. The Ternary Alloys of Magnesium, Zinc, and Cadmium	ii, 51
FRANKLIN (EDWARD CURTIS). Action of Potassium Amide on Thallium Nitrate in Liquid Ammonia Solutions	ii, 52
SCHREINEMAKERS (FRANS A. H.) and (MISS) W. C. DE BAAT. The Quaternary System $KCl - CuCl_2 - BaCl_2 - H_2O$	ii, 53
KREMANS (ROBERT) and F. NOSS. Mutual Solubilities of Cuprous Chloride and Ferrous Chloride, as also of Cuprous Chloride and Sodium Chloride, and the Transformation Point of $F_2Cl_2 \cdot 4H_2O \rightleftharpoons F_2Cl_2 \cdot 2H_2O + 2H_2O$	ii, 53
BEADURI (KSHITIBHUSHAN). Ammoniacal Sodium Cuprous Trithionate	ii, 53
SCHREINEMAKERS (FRANS A. H.) and J. C. THOMAS. The System $HgCl_2 - CuCl_2 - H_2O$	ii, 54
SLADE (ROLAND EDGAR). The Acid Dissolution Constant of Aluminium and Zinc Hydroxides	ii, 54
WYNTER (L.). Ultramarine Compounds	ii, 54
WEDERIND (EDGAR). The Heuser Ferromagnetic Alloys of Manganese	ii, 55
PAPAYANOS (NICOLA). Ternary Alloys of Iron-Manganese-Copper	ii, 55
FAXTER (GREGORY P.) and CHARLES RUGLAS HOOVER. Revision of the Atomic Weight of Iron. V. Analysis of Ferric Oxide	ii, 55
SMITS (ANDRÉAS). The System Iron-Carbon. III.	ii, 56
LOESE (RICHARD) and E. BECKER. The System Iron-Iron Sulphide	ii, 56
BERGSTÄLLER (SIEGFRIED). Stability of the Oxides of Cobalt in the Interval from Co_2O_3 to CoO	ii, 57
FRATRY (VLADIMIR) and B. ZERAGIN. The Replacement of Metals from Aqueous Solutions of their Salts by Hydrogen at High Temperatures and Pressures. IV.	ii, 57
BERGSTÄLLER (SIEGFRIED). The Origin of the Colour Produced by Cobalt Solutions in Certain Mineral Colours	ii, 58
PAPAYANOS (NICOLA). Ternary Alloys of Nickel-Manganese-Copper	ii, 58
KOPPEL (IVAN). The Constitution of the Hydrogen Compounds of Bivalent Molybdenum	ii, 58
WEMPE (GEORG). Molybdates	ii, 58
ROSENHEIM (ARTHUR) and JOHANNES JAENCKE. Iso- and Hetero-polyacids. VI. Hydrates of Some Hetero-polyacids	ii, 59
COLANI (A.). Action of Acids on Uranoous Oxide	ii, 60
ANDERLINS (L'ATSCHELOFF W.). Assessed Explosibility of Uranyl Nitrate	ii, 60
REINDERS (WILLEM) and S. DE LANGE. The System Thalline-Iodine	ii, 60
AUERBACH (ERNST B.) and K. LANGE. The Volatilisation of Valadic Acid by Halogens	ii, 60

	PAGE
PRANDTL (WILHELM) [with SIGMUND PERKOWSKI]. Hetero-poly-acids Containing Vanadic Acid	ii, 61
HANKROT (MAURICE) and FRANÇOIS RAGULT. Chemical Reactions of β-Gold and Crystallised Gold	ii, 61
SKITA (ALADAR) and W. A. MEYER. The Preparation and Application of Colloidal Platinum Metals	ii, 62
HOFMANN (KARL A.). Osmium Tetroxide as an Oxygen-carrier and the Activation of Chlorate Solutions	ii, 62

Mineralogical Chemistry.

KRUEMMER (A. W.) and R. EWALD. Origin of Native Sulphur	ii, 63
CHARITSCHIKOFF (K. W.). Asphalt Theory of the Formation of Naphtha	ii, 63
JEŽEK (B.). Vrbaita, a New Thallium Mineral from Allechar, Macedonia	ii, 63
KREHLIK (FR.). Chemical Examination of Vrbaita	ii, 63
DOSS (BRUNO). Iron Sulphide in the Miocene Clays of Govt. Samara, Russia	ii, 64
KISPAČIĆ (MIJAT). Bauxite of the Croatian Karst and its Origin	ii, 64
BESBORODKO (N.). A New Deposit of Chrome-iron-ore in Northern Caucasus	ii, 64
CHAPMAN (MILDRED B.). Carboniferous Limestones of the Avon Gorge, Bristol	ii, 65
BUSZ (KARL). Tsumebite, a New Lead Copper Phosphate	ii, 65
FUKUCHI (NOBUYO). Ludhamite from Ashio, Japan	ii, 65
WASHINGTON (HENRY S.). The Constitution of Some "Salic" Silicates	ii, 66
SATŌ (DENZŌ). Sinter from the Geyser of Obama, Japan	ii, 66
CESARO (GIUSEPPE). A Felspar of Porto-Senno (Sardaigne)	ii, 66
HUTCHINSON (ARTHUR) and WALTER CAMPBELL-SMITH. Sericite from North Wales: Kennibrite and Labradorite from Ireland	ii, 66
FUKUCHI (NOBUYO). Laumontite from Ashio, Japan	ii, 67
OKAMOTO (YOSHACHIRO). Minerals of Taiwan (= Formosa)	ii, 67
SCHALLER (WALDEMAR T.). The Tourmaline Group	ii, 68
LACROIX (ALFRED). Minerals from the Pegmatite of Ampangabo, Madagascar	ii, 69
TUČAN FRANČO. Nature and Origin of "Terra rossa"	ii, 69
HUGHES (JOHN O.). Analysis of Red Earth from the Floor of an Ancient Hill	ii, 70
CHIKASHIGE (MASUMI) and TADASHI HIKI. A New Fall of Meteoric Iron in Japan	ii, 70
MERRILL (GEORGE P.). Meteoric Fall near Holbrook, Arizona	ii, 71
PIOR (GEORGE T.). Meteoric Stones of El Nakla El Baharia (Egypt)	ii, 71
WAKIMIZU (TETSUO). Meteorite Fall in Central Japan	ii, 72

Analytical Chemistry.

DITTEICH (MAX) and W. EISEL. The Estimation of Water and of Carbon Dioxide in Minerals and Rocks	ii, 72
DENIGES (GEORGES) and L. CHILLE. New Reagent for Chlorine and Bromine, Free and Combined	ii, 72
GOOCH (FRANK A.) and P. L. BLUMENFELD. The Iodic Acid Process for the Estimation of Bromine in Halogen Salts	ii, 73
SCHWAB (L.) and GEORG MÜNCHMEYER. Oxidizable Substances in the Air	ii, 73
WINTERSTEIN (HANS). An Apparatus for Microanalysis of Gases and Micro-spectrometry	ii, 73
MENKE (J. B.). Estimation of Tellurium by means of Hydroxide Hydrate	ii, 74
ZELINKER (H.). Detection of Nitrogen in Organic Substances	ii, 74
BAUDSCH (OSKAR) and GABRIEL KLINGNER. A New Gas-analytical Method for the Estimation of Nitric Oxide. I.	ii, 74

	PAGE
PRIMOZ. Detection of Nitrous Acid in Water	ii, 75
CAVAZZA (LUIGI ERMANN). Estimation of Nitrates with Indigo	ii, 75
LOCKMANN (GEORG). The Marsh Arsenic Test	ii, 75
BRUNCK (OTTO). Estimation of Small Quantities of Carbon Monoxide	ii, 75
FORBES (W. R.). Simple Apparatus for the Estimation of Carbon Dioxide	ii, 75
MACDOUGALL (F. H.). Cobaltinitrite Method of Estimating Potassium	ii, 76
CURTMAN (LOUIS J.) and A. D. ST. JOHN. Determination of the Sensitivity of the Hydroxide Reactions for the Common Metals	ii, 76
UTZ (FRANZ). Estimation of Lead in Lead Paints	ii, 76
KOHN (MORITZ) and ARTHUR KLEIN. Cuprous Iodide	ii, 76
CURTMAN (LOUIS J.) and A. D. ST. JOHN. Sensitiveness of the Bead and Lead Dioxide Tests for Manganese with Special Reference to the Interference of Iron	ii, 77
KÖNIG (F.). Estimation of Iron in Water	ii, 77
FORTINI (V.). Reagent for Detecting Small Quantities of Nickel	ii, 77
HAUSER (OTTO) and H. HENZFELD. Test for Methane, I.	ii, 77
ROUTALA (OSCAR). Analysis of Hydrocarbon Mixtures	ii, 78
WEISHUT (FRITZ). Methoxyl Estimation with Hydriodic Acid and Phenol	ii, 78
FELLENBERG (THEODORE VON). Estimation of Higher Alcohols in Wine	ii, 78
FELLENBERG (THEODORE VON). A Colour Reaction of Wine	ii, 78
FELLENBERG (THEODORE VON). Examination of Lead Precipitates in Wine; Pentose and Methylpentose Estimations in Grapes and Wine	ii, 79
OCHSNER DE CONINCK (WILLIAM). A Simple Method of Characterising Acetaldehyde	ii, 79
MÄDER (H.). A Bromometric Estimation of Formic Acid	ii, 79
HARDING (VICTOR JOHN) and ROBERT FULFOLD RUTTAN. The Detection of Acetoacetic Acid by Sodium Nitroprusside and Anmonia	ii, 79
SCHMATOLLA (OTTO). Detection of Benzole Compounds	ii, 79
CHARITSCHIKOV (K. W.). Nature of the Reactions of Naphthenic Acids	ii, 80
FOLIN (OTTO) and A. B. MACALLUM, jun. A New Method for the Colorimetric Estimation of Uric Acid in Urine	ii, 80
EYERS (NORMAN). Detection and Estimation of Arachis Oil	ii, 80
WEISSER (FRANZ). Estimation of Cyanogen Compounds in Gas-Liquors	ii, 81
MOLWES (CURT). Estimation of Scetole and Indole in Faeces	ii, 81
KOHN-ABREST (EMILE). Action of Activated Aluminium on Alkaloidal Extracts. Its Use in Toxicology	ii, 81
SCHERRATSCHEV (D.). Distinction between Cocaine and its Substitutes	ii, 82
KREYSSE (P. J.). Gravimetric Estimation of Quinine as Nitroprusside	ii, 82
KREYSSE (P. J.). Estimation of Quinine Sulphate in Cinchona Bark	ii, 82
SEGMUND (WILHELM). Hyposulphite in Volumetric Analysis. I.	ii, 82
KOLSAKOV (MILÉ MARIE). Methods of Estimating Saponins	ii, 83
JOLLES (ADOLF). A Delicate Test for the Detection of Albumin in Urine	ii, 83
REBER (M. L.). Chemistry and Estimation of Gelatin	ii, 83
WALKER (J. T. AINSIE) and JOHN M. WEISS. The Rideal-Walker Phenol Control. A Possible Discordant Factor in the Standardisation of Disinfectants	ii, 84

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS

A.

Abderhalden, E., and E. Wurm, i, 23.
90.
Abelin, J., i, 136.
Aboulenc, J. See J. B. Senderens.
Acker, E. See F. Kehrman.
Aegna, C., i, 147.
Agulhon, H., and R. Suz-rac, i, 143.
Alexander, P., i, 67.
Alterthum, H., ii, 16.
Alvisi, U., i, 151.
Ammann, L. See L. Lindet.
Anderson, R. J., i, 149.
Andrews, L. W., ii, 69.
Angelico, F., i, 69.
Anrep, G. von, i, 121.
Arndt, K., and H. H. Kunze, ii, 48.
Arnold, V., i, 111.
Aschurim, P. See A. E. Favorski.
Aton, A. H. W., ii, 40.
Auerbach, E. B., and K. Lange,
ii, 60.

B.

Baat, (Miss) W. C. de. See F. A. H.
Schreinemakers.
Back, E. See F. Paschen.
Backman, E. L., i, 129.
Badische Anilin- & Soda-Fabrik,
i, i, 13, 61, 82, 96, 190.
Baister, L. S., and B. D. Steele,
ii, 15.
Bairsto, G. E., ii, 10.
Ballo, R., and E. Dittler, ii, 51.
Bain, E. C. C., and E. O. Rice,
TRANS., 91.
Bang, L., i, 111.
Bargellini, G., and M. Finkelstein,
i, 59.
Bargellini, G., and E. Martegiani,
i, 99.
Bart, H., i, 115.

Batschinski, A. J., ii, 26.
Battelli, F., and (Mile.) L. Stern,
i, 115, 139, 140.
Baud, E., ii, 19.
Baudisch, O., i, 52.
Baudisch, O., and R. Fürst, ii, 38.
Baudisch, O., and G. Klinger,
ii, 71.
Baur, E., and H. Ehrenberg, ii, 13.
Baxter, G. P., and C. R. Hoover,
ii, 55.
Baxter, G. P., and C. J. Moore,
ii, 43.
Beckel, A., i, 56.
Becker, E. See R. Loche.
Beckmann, E., ii, 19, 20.
Behrend, R., and G. ten Doornkaat,
Kodman, i, 8.
Bell, E. T., i, 135.
Bellucci, L., ii, 28.
Berg, W. N., i, 132.
Bergen, J. von. See A. Skita.
Berggren, T. See H. von Euler.
Bergman, M. See J. Schmidlin.
Berlin, E., ii, 38.
Bernar, W., ii, 83.
Berthelot, D., and H. Gaudeloch,
i, 10; ii, 4.
Besborocko, N., ii, 64.
Beutner, R., i, 147.
Beyer, A. See F. Kehrman.
Bhadari, K., ii, 53.
Bianchi, G., and M. Rocchi, i, 96.
Bierry, H., V. Henri, and A. Rane,
ii, 4.
Biesalski, E. See O. Hauser.
Birchard, E. J. See P. A. Levene.
Bistrzecki, A., and G. Piz-worski,
i, 103.
Bjerrum, N., ii, 21.
Blackadder, T., ii, 35.
Blaise, E. E., i, 11.
Blanksma, J. J., i, 11, 31.
Blumenthal, P. L. See F. A. Gooch.

Böck, F., and L. Moser, ii, 9.
 Boeseken, J., i, 43.
 Boeseken, J., and M. Cluwen, i, 6.
 Bogert, M. T., and H. L. Fisher, i, 98, 109.
 Boudy, R. See H. Meyer.
 Bookman, S. See A. A. Epstein.
 Boothby, W. M., i, 120.
 Bornhardt, C. See W. Schlenk.
 Bostock, G. D., i, 131.
 Boulanger, C., and G. Urbain, ii, 34.
 Boutaric, A., ii, 21.
 Bounty, E., ii, 10.
 Brenning, E. See A. Thiel.
 Bridel, M., i, 149, 150.
 Bridgman, P. W., ii, 39.
 Brilliant, G. See A. E. Favorski.
 Briner, E., ii, 21.
 Brown, F. C., ii, 8.
 Brühl, (Mlle.) H., ii, 50.
 Brunck, O., ii, 75.
 Brum, G., and C. Sandonini, ii, 51.
 Buiow, C., i, 101.
 Burkner, K., i, 110.
 Burgetaller, S., ii, 57, 58.
 Burridge, W., i, 129.
 Burrows, G. H. See G. N. Lewis.
 Burton-Opitz, R., i, 138.
 Buschmann, E., i, 148.
 Busz, K., ii, 65.
 Bygden, A., i, 29.

C.

Campbell-Smith, W. See A. Hutchison.
 Carbone, D., and G. Pighini, i, 128.
 Carpinux, E. See A. Gregoire.
 Cassella & Co., L., i, 28.
 Cathcart, E. P., and J. Henderson, i, 126.
 Cavazza, L. E., ii, 75.
 Cerverio, C., and C. Varvaro, i, 109.
 Cesaris, M., i, 99.
 Cesaro, G., ii, 66.
 Chandelon, T., i, 18.
 Chapman, M. B., ii, 65.
 Charitshanova, M. See A. E. Favorski.
 Charitshkov, K. W., ii, 63, 62.
 Charpentier, See L. Linden.
 Chelle, L. See G. Deniges.
 Chemische Fabrik und Aktien-Verein, Schering, i, 5, 92.
 Chemische Fabrik Griesheim-Elektron, i, 107.
 Chikashige, M., and T. Hiki, ii, 70.

Chistoni, A., i, 140.
 Christiansen, J., i, 112.
 Clark, A. J., i, 130.
 Clifford, O. C. See A. A. Knowlton.
 Cluwen, M. See J. Boeseken.
 Colani, A., ii, 90.
 Colver-Glauret, E. See (Sir) R. Hadfield.
 Cone, L. H., i, 92.
 Corriez, L., i, 89, 90.
 Crommelin, C. A., ii, 20.
 Crowther, H. L., and R. McCombie, Trans., 27.
 Cumming, A. C., ii, 14.
 Curtman, L. J., and A. D. St. John, ii, 76, 77.

D.

Dahn, A. See T. Zincke.
 Dale, H. H., i, 132.
 Danckworth, P. W., i, 87.
 Davidsohn, H., i, 123.
 Davidsohn, H. See also L. Michaelis.
 Delezenne, C., and (Mlle.) S. Ledebur, i, 117.
 Deniges, G., and L. Chelle, ii, 72.
 Denis, W., i, 123.
 Denison, R. B., ii, 36.
 Decenter, C. M. van, ii, 14.
 Dhar, N. See P. C. Ray.
 Dieckmann, T. See Sir R. Hadfield.
 Dittler, E. See R. Baillo.
 Dittrich, M., and W. Eitel, ii, 72.
 Dixon, W. E., and W. E. Lee, i, 139.
 Dixon, W. E., and F. Ransom, i, 129.
 Dobbie, J. J., J. J. Fox, and A. J. H. Grieve, Trans., 36.
 Dönnikrat Koorman, G. ten. See R. Bickton.
 Doss, E., ii, 64.
 Douma, R., and A. Wirth, i, 79.
 Dox, A. W., and R. E. Neiding, i, 142.
 Drescher, A. H. See E. V. McGillem.
 Duane, W., ii, 7.
 Ducloux, J., ii, 18.
 Dunstan, A. E., T. P. Hilditch, and F. B. Thole, Trans., 134.
 Dunstan, A. E., and F. B. Thole, Trans., 127.
 Dupont, L. L., and A. Portevin, ii, 19.

E.

E. Aert, A. See H. Meyer.
 Eisenberg, H. See E. Mann.
 Eisen, E., i, 85.

Eitel, W. See M. Dittrich.
 Euklaar, J. E., ii, 29.
 Epstein, A. A., and S. Bookman,
 i, 139.
 Euler, H. von, and T. Berggren,
 i, 145.
 Evers, N., ii, 80.
 Ewald, R. See A. W. Kruemmer.
 Ewins, A. J., TRANS., 97.
 Ewins, A. J., and H. King, TRANS.,
 104.

F.

Falek, O. See W. Pauli.
 Farbenfabriken vorm. F. Bayer
 & Co., i, 1, 2, 31, 61, 63, 95, 96, 105,
 108, 118.
 Farbwerte vorm. Meister, Lucius
 & Brünig, i, 83, 95, 96, 100, 105,
 110, 117.
 Farrow, F. D. See R. E. Slade.
 Favorski, A. E., P. Aschmarin,
 G. Brilliant, M. Charitonova, E.
 Fricman, I. Idelson, B. Isat-
 schenko, (Mlle.) S. Kolotova,
 N. Mandryk, D. Seiborski,
 (Mlle.) A. Umnova, A. Vansh-
 chik, T. Velitschkovski, and
 (Mlle.) A. Zacharova, i, 12.
 Feist, K., i, 70.
 Fellenberg, T. von, ii, 78, 79.
 Fernon, D., i, 126.
 Ferry, (Miss) E. L. See T. B.
 Osborne.
 Fichter, F., ii, 78.
 Finkelstein, M. See G. Pargellind.
 Fischer, H., and E. Krollschitten,
 i, 33.
 Fischer, H., and E. Meyer-Behn,
 i, 111.
 Fischer, H., and H. Rose, i, 71.
 Fisher, H. L. See M. T. Bagert.
 Fitzgerald, F. F., ii, 32, 33.
 Folin, O., and H. Lyman, i, 126.
 Folin, O., and A. B. May, TRANS.,
 ii, 29.
 Forbes, W. R., ii, 75.
 Forster, M. O., and H. A. H.
 Howard, TRANS., 95.
 Fortini, V., ii, 77.
 Fosse, R., i, 72.
 Fouassier, M. See A. Trillat.
 Fournneau, E., and A. Villa, i, 117.
 Fox, J. J. See J. J. Dobbie.
 Frankel, S., P. Kirschbaum, and K.
 Linbert, i, 128.
 Franke, A., and G. Kienberger, i, 1.
 Franke, A., and A. Kien, i, 10.
 Franklin, E. C., ii, 52.
 Freund, E., and G. Kaminer, i, 135.
 Fricman, E. See A. E. Favorski.

Friedrich, K., ii, 27.
 Friedrich, K., and L. G. Smith,
 ii, 28.
 Fürst, R. See O. Baudisch.
 Fukuchi, N., ii, 65, 67.
 Fulleher, G. S., ii, 5.
 Fuld, E., and E. Schlesinger,
 i, 122.

G.

Garcia-Bandis, A. See J. Schmidlin.
 Garver, M. M., ii, 24, 25.
 Gaudechon, H. See D. Berthelot.
 Gange, A. J. H. See J. J. Dobbie.
 Gebhard, K., i, 28.
 Gehlhoff, G., ii, 9.
 Gehrcke, E., and R. Seeliger, ii, 5.
 Gérard, P. J., i, 120.
 Gerhardt, W., i, 47.
 Gibson, G. E. See A. Stock.
 Gillespie, L. J. See F. G. Keyes.
 Giller, A., ii, 28.
 Gin, G., i, 152.
 Ginncken, P. J. H. van, i, 16.
 Givens, M. H. See A. Hunter.
 Gnaedinger, J. See F. Ullmann.
 Gobel, J. B., ii, 34.
 Goerens, P. See E. Gumlach.
 Goldschmidt, G., i, 71.
 Goldschmidt, G., and E. Zerner,
 i, 9.
 Goldberg, M., and C. J. West, i, 72.
 Goldsch, P. A., and P. L. Blumen-
 thal, ii, 73.
 Gortner, K., i, 148.
 Grate, L., i, 125.
 Grate, V., i, 69.
 Grate, V., and V. Vauk, i, 118.
 Gratzdyk, (Mlle.) L. M., ii, 1.
 Gramschitzky, M., i, i, 127.
 Granchowicz, E., i, 132.
 Gray, J. G., and A. D. Ross, ii, 18.
 Gratzke, A., and E. Carpiat,
 i, 132.
 Grigorova, N. See A. von Lebedev.
 Gruber, M., i, 132.
 Gumlach, E., and P. Goerens, ii, 17.
 Günther, M. See F. Kellmann.
 Gutmann, S. See W. L. de

H.

Haus, G., i, 139.
 Heilmann, Sir R., E. Colver-Glad-
 ston, E. Dieckmann, F. Heuston,
 S. Hilpert, K. Ornes, A. D. Ross,
 E. Take, E. Wedekind, and E.
 Weiss, ii, 17.
 Heilmann, J., i, 133.
 Haldane, J. B. S., i, 122.
 Halpin, J. G. See E. V. McCollum.

- Hauriot, M., ii, 26.
 Hauriot, M., and F. Raoult, ii, 61.
 Harding, V. J., and R. F. Ruttan, ii, 79.
 Hart, E. B., G. C. Humphrey, and F. B. Morrison, i, 151.
 Hasselbalch, K. A., i, 119.
 Hauser, O., and E. Biesalski, i, 26.
 Hauser, O., and H. Herzfeld, ii, 77.
 Hedin, S. G., i, 114.
 Heimann, W., See L. Mohr.
 Henderson, J., See E. P. Cathcart.
 Henjes, F., See O. Wallach.
 Henri, V., See H. Bierry.
 Herz, W., and F. Kuntze, ii, 33.
 Herz, W., and W. Kathmann, ii, 26.
 Herzenstein, A., See W. Schlenk.
 Herzfeld, H., See O. Hauser.
 Heublein, O., See J. Tillmans.
 Heusler, F., See (Sir) R. Hadfield.
 Hevesy, G. von, and R. E. Slade, ii, 13.
 Heyl, R. Cison, i, 114.
 Hibi, T., See M. Chikashige.
 Hibbitch, T. P., See A. E. Dunstan.
 Hipert, S., See (Sir) R. Hadfield.
 Hixson, G. I., 123.
 Hochstetter, A., See R. Schenckle.
 Hofmann, K. A., ii, 92.
 Hollmann, A. F., i, 39.
 Holmberg, B., i, 7.
 Homann, W., See E. Vongerichten.
 Hoover, C. R., See G. P. Brayton.
 Hoffmann, P., i, 59.
 Howard, H. A. H., See M. O. Forster.
 Howard, S. E., and H. C. Jones, ii, 11.
 Hughes, J. O., ii, 79.
 Humphrey, G. C., See E. B. Hart.
 Hunter, A., and M. H. Gwynne, i, 126.
 Hutchinson, A., and W. Campbell Smith, ii, 66.
 Hynd, A., See J. C. Irvine.

I.
 Idelson, I., See A. E. Favarski.
 Ipatiev, V. N., and B. Zingagin, ii, 57.
 Ipatiev, V. N., N. Matoy, and O. Rouda, i, 65.
 Ipatiev, V. N., i, 19.
 Irvine, J. C., and A. Hynd, Trans., ii.
 Istratenco, B., See A. E. Favarski.
 Istrati, C. I., and M. A. Mihalcescu, i, 29.
 Itami, S., i, 136.
 Iwanov, N., i, 145.

J.
 Jacobson, C. A., i, 151.
 Jaeger, F. M., and J. B. Menke, ii, 41.
 Jaenicke, J., See A. Rosenheim.
 Johnson Blohm, G., i, 114.
 Juhn, B. C. P., i, 9, 126.
 Jegorov, M. A., i, 146.
 Jezek, B., ii, 63.
 Johndessohn, F., i, 143.
 Jolles, A., i, 9; ii, 83.
 Jones, H. C., See S. E. Howard.
 Jouniaux, H., 29.

K.
 Kallen, A., i, 5; ii, 7, 8.
 Kamm, G., See E. Freund.
 Karvonen, A., ii.
 Katz, J. R., ii, 27.
 Keessig, W. H., ii, 25.
 Kehrman, F., E. Acker, M. Günther, and J. Knoch, i, 77.
 Kehrman, F., and A. Berger, i, 94.
 Kehrman, F., and Z. Matuszsky, i, 93.
 Kehrman, F., and T. E. Stillier, i, 77.
 Kerk, J., See O. Neuberg.
 Keres, F. G., and L. J. Gillespie, ii, 142.
 Kienberger, O., See A. Franke.
 Klein, H., See A. J. Reibens.
 Kirschner, E., See S. F. Lohr.
 Kistner, M., i, 84.
 Kistner, E., i, 47.
 Kitchin, J. G., i, 137.
 Kleeman, E. D., ii, 26.
 Klein, A., See A. Franke and M. Kohn.
 Kleinen, A., ii, 17.
 Kleinen, A., ii, 49.
 Klein, K. G., ii, i, 111.
 Kluge, G., See O. Bandisch.
 Knoll, G., i, 83.
 Knopf, J., See E. Kehrman.
 Knowlton, A. A., and O. C. Clifford, ii, 18.
 Kohn, E., ii, 77.
 Kohn, M., and A. Klein, ii, 76.
 Kohn Alvest, E., ii, 81.
 Korte, W., S. Deschle, and M. Rothemann, i, 136.
 Kolosovska, N., ii, 22.
 Kolotov, M. I., L., See A. E. Favarski.

Komatsu, S., i, 39.
 Korschegg, A. von, i, 131.
 Koppel, I., ii, 58.
 Korsakov, (Mlle.) M., i, 149; ii, 53.
 Kossowicz, A., i, 146.
 Krauch, K. See R. Stollé.
 Krehlik, F., ii, 63.
 Kreman, R., and F. Noss, ii, 53.
 Kreman, R., and R. Schoulz, ii, 15.
 Krösche, W. See C. Mannich.
 Kröllpelffer, F. See H. Fischer.
 Krüger, O. See T. Zincke.
 Krümmmer, A. W., and K. Ewald, ii, 63.
 Krusysse, P. J., ii, 82.
 Küster, E., i, 147.
 Küster, W., i, 110.
 Kunckell, F., and G. Ulex, i, 20.
 Kuntze, F. See W. Herz.
 Kunze, H. H. See K. Arndt.
 Kurilov, B., ii, 31.
 Kylin, H., i, 149.
 Kym, O., and L. Ratner, i, 102.

L.

Laborde, A., and A. Lepape, ii, 9.
 Lacroix, A., ii, 69.
 Lange, K. See E. B. Anerbach.
 Lange, S. See W. W. Reinders.
 Langgaard, A., i, 141.
 Lebedev, A. von, i, 144.
 Lebedev, A. von, and N. Griaznov, i, 144.
 Ledebt, (Mlle.) S. See C. Delezenne.
 Ledoux, R., ii, 19.
 Lee, W. E. See W. E. Dixon.
 Lecaw, H. L. de, ii, 49.
 Leger, E., and F. Raquet, i, 83.
 Lery, D., jun. See W. Reinders.
 Lepape, A. See A. Laborde.
 Levene, P. A., and F. J. Birchard, i, 19.
 Lewis, G. N., ii, 29.
 Lewis, G. N., and G. H. Burrows, ii, 23.
 Lewis, H. B., i, 125.
 Lewis, W. C. McC. See A. P. Roshdestwensky.
 Liebig, H. von, i, 76.
 Liese, E., i, 1.
 Linnet, L., and L. Annamati, i, 143.
 Linnet, L., and J. J. Perpetua, i, 17.
 Linkart, G. A., ii, 35.
 Linnet, K. See S. Frankel.
 Lippmann, E. O. von, i, 159.
 Lockbaum, G., ii, 75.
 Lock, A., i, 153.
 Lock, J., i, 127.

Loeb, W., and S. Gutmann, i, 121.
 Loebe, R., and E. Becker, ii, 56.
 Loew, O., i, 10.
 Loewi, O., i, 129, 130.
 López-Suárez, J., i, 123.
 Lückenheimer, F., ii, 3.
 Lusk, G., and J. A. Riche, i, 123, 124.
 Lyman, H. See O. Folin.

M.

Macallum, A. B., jun. See O. Folin.
 McCollum, E. V., A. H. Drescher, and J. G. Halpin, i, 132.
 McCollum, E. V., and H. Steenbock, i, 125.
 McCombie, H., and H. A. Scarborough, TRANS., 56.
 McCombie, H. See also H. L. Crowther.
 McCutcheon. See A. Werner.
 MacDougall, F. H., ii, 76.
 McKenzie, A., and G. Martin, TRANS., 112.
 Madelung, W., i, 91.
 Mader, H., ii, 79.
 Maillie, A., i, 44.
 Mair, L. See W. Schlenk.
 Mameli, E., i, 47.
 Mameli, E., and A. Mannessier, ii, 19.
 Mandryk, N. See A. E. Favorski.
 Mannessier, A. See E. Mameli.
 Mannich, C., i, 87.
 Mannich, C., and W. Krösche, i, 191.
 Marchlewski, L., i, 110.
 Mariouda, P., i, 126.
 Marinisco, G., i, 128.
 Marignani, E. See G. Bargellini.
 Martin, G., TRANS., 119.
 Martin, G. See also A. McKenzie.
 Marx, E. See W. Zaleski.
 Massena, C. See A. Stock.
 Masson, G., i, 68.
 Math, M., i, 48.
 Matro, N. See V. N. Ipatiev.
 Mathusinsky, Z. See F. Kehrman.
 Mathney, F., i, 59.
 Maximov, N. A., i, 159.
 Mellanby, J., i, 114.
 Mellanby, J., and V. J. Woodley, i, 113.
 Menzel, L. R. See T. B. Osborne.
 Meneghini, D., ii, 19.
 Mengo, O., ii, 34.
 Menke, J. B., ii, 41, 74.
 Menke, J. B. See also F. M. Juelzer.
 Meerk, E., i, 5.
 Merz, G. P., ii, 71.
 Merton, T. E., TRANS., 124.
 Metten, J., ii, 24.

Meyer, F., and A. Stähler, ii, 48.
 Meyer, G. A. See D. Vorländer.
 Meyer, H., R. Bondy, and A. Eckert, i, 62.
 Meyer, W. A. See A. Skita.
 Meyer-Betz, F. See H. Fischer.
 Meyerhof, O., i, 146.
 Michaelis, L., ii, 31.
 Michaelis, L., and H. Davidsohn, i, 121.
 Michaelis, L., and H. Pechstein, i, 109.
 Micklethwait, (Miss) F. M. G. See G. T. Morgan.
 Mihailesen, M. A. See C. I. Istrati.
 Milikan, J., i, 24.
 Milo, C. J., i, 152.
 Mchlan, R., i, 104.
 Moewes, C., ii, 81.
 Mohr, L., and W. Heilmann, i, 132.
 Moll van Charante, J. See P. J. Montagne.
 Montagne, P. J., and J. Moll van Charante, i, 55.
 Moore, C. J. See G. P. Baxter.
 Morgan, G. T., and (Miss) F. M. G. Micklethwait, *TRANS.*, 71.
 Morgan, G. T., and H. W. Moss, *TRANS.*, 78.
 Morgan, W. C., ii, 41.
 Morrison, F. B. See E. B. Hart.
 Moser, L. See F. Beck.
 Moss, H. W. See G. T. Morgan.
 Mottram, V. H., i, 124.
 Mouren, C., and A. Valeur, i, 89.
 Muller, C., ii, 39.
 Muller, R. See O. Wallach.
 Münchmeyer, G. See L. Schwarz.
 Müller, J. A., ii, 11, 31.
 Mumm, O., i, 59.
 Musciclaun, C. See A. Wehneit.

N.

Neidig, R. E. See A. W. Dux.
 Nenberg, C., and J. Korb, i, 145.
 Newell, C. R. See L. E. Rettger.
 Nichols, E. H. See W. R. Orndorff.
 Nigzli, P., ii, 33.
 Nord, F. See A. Skita.
 Noss, F. See R. Krimann.
 Notting, P., i, 152.

O.

Obulensky, W., ii, 3.
 Oechslin de Coninck, W., ii, 51, 59.
 Oesterle, O. A., i, 149.
 Ohta, K., i, 121.
 Okamoto, Y., ii, 67.
 Onnes, K. See (Sir) R. Hadfield.

Oosterhuis, E., ii, 13.
 Orelkine, B. See J. Tschugaev.
 Orlov, N. A., i, 27.
 Orndorff, W. R., and E. H. Nichols, i, 99.
 Osborne, T. B., L. B. Mendel, and (Miss) E. L. Ferry, i, 124.
 Ostrogovich, A., i, 197.
 Ostwald, W., ii, 32.

P.

Palitzsch, S., and L. G. Walbum, i, 112.
 Palomaa, M., i, 6.
 Panzer, T., i, 113.
 Parravano, N., ii, 33, 55, 58.
 Paschen, F., and E. Back, ii, 2.
 Patta, A., i, 125.
 Pauli, W., and O. Falek, i, 168.
 Pechstein, H. See L. Michaelis.
 Pellet, H., i, 151.
 Perkowski, S. See W. Prandtl.
 Perman, E. P., and T. W. Price, ii, 20.
 Peschie, S. See W. Kollé.
 Peters, W., ii, 42.
 Petrenko-Krutschenko, P. I. See J. Schottlé.
 Petterson, L., i, 27.
 Philippson, M., ii, 32.
 Piccard, A. See P. Weiss.
 Pighini, G. See D. Carbone.
 Pihlblad, N., ii, 2.
 Portevin, A. See E. L. Dupuy.
 Praetorius, P. See A. Stock.
 Prager, W., i, 5.
 Prandtl, W., and S. Perkowski, ii, 61.
 Pradsnitz, P. H., ii, 39.
 Price, T. W. See E. P. Perman.
 Primot, ii, 75.
 Prior, G. T., ii, 71.
 Przeworski, G. See A. Bistrzycki.

R.

Racky, G. See W. Schlenk.
 Radulescu, D., i, 37; ii, 67.
 Rakshit, J. N. See P. C. Ray.
 Rane, A. See H. Bierry.
 Ransom, F. See W. E. Dixon.
 Raoult, F. See M. Hauriol.
 Rathmann, W. See W. Herz.
 Rather, L. See O. Kym.
 Ray, P. C., and N. Dhar, *TRANS.*, 3, 10.
 Ray, P. C., and J. N. Rakshit, *TRANS.*, 1.
 Reichenberg, W. von. See O. Wallach.

- Reinders, W., and S. de Lange, ii, 60.
 Reinders, W., and D. Lely, jun., ii, 33.
 Renning, J. See W. Schlenk.
 Rettger, L. F., and C. R. Newell, i, 143.
 Reuss, F. See H. Stobbe.
 Reutter, L., i, 67, 68.
 Reyher, A., i, 6.
 Rice, F. O. See E. C. C. Baly.
 Riche, J. A. See G. Lusk.
 Riedel, J. D., i, 63.
 Ringer, W. E., and J. I. J. M. Schmutzer, i, 168.
 Risse, F. See F. W. Semmler.
 Robertson, T. B., i, 122.
 Rocchi, M. See G. Bianchi.
 Röse, H. See H. Fischer.
 Rohland, P., ii, 27.
 Rous, P., i, 127.
 Roques, F. See E. Léger.
 Rosenheim, A., and J. Jaenicke, ii, 59.
 Rohestwensky, A. P., and W. C. McC. Lewis, ii, 13.
 Ross, A. D. See J. G. Gray, and Sir R. Hadfield.
 Rothermund, M. See W. Kelle.
 Routsala, O. See 78.
 Routsala, O. See also V. N. Ipatiev.
 Rowe, A. H., i, 132.
 Ruthertford, E., ii, 4.
 Ruttan, R. F. See V. J. Harding.
- S.**
- St. John, A. B. See L. J. Curtman.
 Stacey, M., i, 17.
 Sandonini, C. See G. Bruni.
 Sato, D., ii, 66.
 Santon, B., i, 116.
 Sazerac, R. See H. Agulhon.
 Scaffidi, V., i, 126.
 Scarborough, H. A. See H. McCumbie.
 Schaarschmidt, A., i, 194.
 Schaarschmidt, A., and A. Stahl-schmidt, i, 95.
 Schaller, W. T., ii, 28.
 Scheffer, F. E. C., ii, 22.
 Schelenz, H., i, 2.
 Scherbatschev, D., ii, 82.
 Schestakov, P. J., i, 97.
 Scheuble, R., and A. Hochstetter, i, 4.
 Schleicher, A. P., ii, 19.
 Schlenk, W., C. Bornhardt, A. Herzenstein, L. Mair, G. Rucky, and J. Renning, i, 34.
 Schlesinger, E. See E. Fuld.
 Schmatolla, O., ii, 79.
 Schmidlin, J., i, 32.
 Schmidlin, J., and M. Bergman, i, 46.
 Schmidlin, J., and A. Garcia-Banús, i, 33, 50.
 Schmidt, E., and A. Seeberg, i, 19.
 Schmutzer, J. I. J. M. See W. E. Ringer.
 Schoeller, W., and W. Schrauth, i, 119.
 Schottle, J., and P. I. Petrenko-Kritschenko, i, 48.
 Scholl, R., C. Seer, and O. von Seybel, i, 56.
 Scholtz, M., i, 87.
 Schoultz, R. See R. Kremann.
 Schrauth, W. See W. Schoeller.
 Schreinemakers, F. A. H., and (Miss) W. C. de Baat, ii, 53.
 Schreinemakers, F. A. H., and J. C. Thonns, ii, 54.
 Schübel, K., i, 133.
 Schuly, L., i, 147.
 Schulz, H., i, 131.
 Schwarz, L., and G. Münchmeyer, ii, 73.
 Schwarzkopf, P., i, 26.
 Seiborski, D. See A. E. Favorski.
 Sehor, J. See J. Stoklasa.
 Seeberg, A. See E. Schmidt.
 Seeltiger, R. See E. Gehrke.
 Seer, C. See R. Scholl.
 Semmler, F. W., and F. Risse, i, 96.
 Sanderens, J. B., and J. Aboulene, i, 41, 42.
 Seybel, O. von. See R. Scholl.
 Shibata, Y. See A. Werner.
 Siegfried, M., and R. Zimmermann, i, 120.
 Siegmund, W., ii, 82.
 Skita, A., J. von Bergen, W. A. Meyer, and F. Nord, i, 63.
 Skita, A., and W. A. Meyer, i, 53, 54; ii, 62.
 Skórzewski, W., i, 133.
 Skórzewski, W., and J. Sohn, i, 138.
 Slade, R. E., ii, 16, 54.
 Slade, R. E., and F. D. Farrow, ii, 18.
 Slade, R. E. See also G. von Hervey.
 Smiley, (Miss) L., i, 124.
 Smith, L., ii, 35.
 Smith, L. G. See R. Friedrich.
 Smits, A., ii, 56.
 Soddy, F., ii, 4.
 Sohn, J. See W. Skórzewski.
 Stähler, A. See F. Meyer.
 Stahlschmidt, A. See A. Schaarschmidt.

Stamm, E. See A. Stock.
 Stark, J., ii, 2.
 Starkenstein, E., i, 128.
 Steele, B. D. See L. S. Bagster.
 Steenbock, H. See E. V. McCollum.
 Stern, (Mile.) L. See F. Battelli.
 Stern, O., ii, 28.
 Stieglitz, J., ii, 36.
 Stillier, T. E. See F. Kehrman.
 Stobbe, H., and F. Reuss, i, 29.
 Stock, A., G. E. Gibson, and E. Stamm, ii, 43.
 Stock, A., and C. Massenez, ii, 44.
 Stock, A., and P. Praetorius, ii, 46.
 Stockman, R., i, 84.
 Stoklasa, J., J. Šebor, and W. Zdobnický, i, 18.
 Stolb, R., and K. Krauch, i, 97.
 Suida, H., i, 28, 52.
 Swarts, F., ii, 22.

T.

Tafel, J., i, 117.
 Take, E. See (Sir) R. Hadfield.
 Tamman, G., ii, 45.
 Tassart, M., i, 18.
 Taylor, H. S., TRANS., 31.
 Thiel, A., and E. Breuning, ii, 15.
 Thole, F. B., TRANS., 19.
 Thole, F. B. See also A. E. Dunstan.
 Thomas, A. See G. F. White.
 Thonus, J. C. See F. A. H. Schreinemakers.
 Tillmans, J., and O. Heublein, ii, 61.
 Traube, W., ii, 49.
 Tribe, E. M., i, 137.
 Trillat, A., and M. Fouassier, i, 113.
 Tschachotin, S., i, 142.
 Tschernov, G. See A. Werner.
 Tschugaev, J., and B. Orelkine, i, 23.
 Tschugaev, L. A., ii, 3.
 Tschau, F., ii, 69.

U.

Ulex, G. See F. Kunckell.
 Ullmann, F., and J. Guadinger, i, 195.
 Umnova, (Mile.) A., i, 7.
 Umnova, (Mile.) A. See also A. E. Favorski.
 Urbain, G. See C. Boulanger.
 Ute, F., ii, 76.

V.

Valeur, A. See C. Monren.
 Vanschejdt, A. See A. E. Favorski.
 Varvaro, C. See C. Cervello.
 Velitschkovski, T. See A. E. Favorski.
 Vereinigte Chemische Werke Aktiengesellschaft, i, 113.
 Vereinigte Ch�minfabriken Zimmer & Co., i, 85.
 Viehoever, A., i, 142.
 Vila, A. See E. Fourneau.
 Viquerat, A., i, 23.
 Volmer, M., ii, 6.
 Vongerichten, E., and W. Homann, i, 39.
 Vorlander, D., and G. A. Meyer, i, 56.
 Vouk, V. See V. Gratz.
 Vournasos, A. C., i, 25.

W.

Wakimizu, T., ii, 72.
 Walbaum, L. G. See S. Palitzsch.
 Walker, J. T. A., and J. M. Weiss, ii, 81.
 Wallach, O., F. Henjes, and E. Müller, i, 63.
 Wallach, O., and W. von Rechenberg, i, 54.
 Wartenberg, H. von, ii, 47.
 Washington, H. S., i, 65.
 Weber, K. H., ii, 15.
 Welekind, E., ii, 55.
 Welekind, E. See also (Sir) R. Hadfield.
 Weevers, T., i, 147.
 Wehnelt, A., and C. Muscclmann, ii, 23.
 Weigert, F., ii, 3.
 Weimann, P. P. von, ii, 31, 52.
 Weisheit, F., ii, 78.
 Weiss, J. M. See J. T. A. Walker.
 Weiss, P., and A. Piccard, ii, 17.
 Weiss, P. See also (Sir) R. Hadfield.
 Weisser, F., ii, 81.
 Wempe, G., ii, 58.
 Werner, A., and McCutcheon, i, 19.
 Werner, A., and Y. Shibata, i, 22.
 Werner, A., and G. Tschernov, i, 23.
 West, C. J. See M. Gomburg.
 White, G. F., and A. Thomas, i, 123.
 Wiener, H., i, 122.
 Wilgows, H. S., ii, 4.
 Winterstein, H., ii, 73.
 Wirth, A. See R. Davis.

- Wolff, J., i, 115.
 Woolley, V. J. See J. Mellanby.
 Worden, E. C., i, 19.
 Wunder, L., ii, 54.
 Wurm, E. See E. Abderhalden.
- Z.**
- Zacharova, (Mlle.) A. See A. E. Favorski.
 Zaleski, W., and E. Marx, i, 148.
 Zdobnický, W. See J. Stoklasa.
 Zellner, H., ii, 74.
 Zerner, E. See G. Goldschmidt.
 Zimmermann, R. See M. Siegfried.
 Zincke, T., and A. Dahm, i, 45.
 Zincke, T., and O. Krüger, i, 44.
 Zrjagin, B. See V. Ipatiev.
 Zuz, E., i, 108.
 Zweigbergk, N. von, i, 24.

ERRATUM.

VOL. CH (ABSTR., 1912).

Page.	Line.
ii, 243	12.* $f(x) = \int_0^x K(t) dt = \int_0^x (A + tB) dt = \frac{1}{2} K(x) + \frac{1}{2} K(0) + A \cdot x$.

* From bottom.

JOURNAL
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TRANSACTIONS.

1. Nitrites of the Alkyllic Ammonium Series. Nitroso-piperazinium Nitrite.

By PRAFULLA CHANDRA RAY and JIJENDRA NATH RAJSHI.

In previous communication, it has been shown that the alkylamines of the primary, secondary, and tertiary series invariably give the corresponding nitrites. The investigation has now been extended to the members of the allylic groups, and piperazine was selected as a typical representative.

Following the general method, piperazinium chloride solution was treated with silver nitrite, and the nitrite was evaporated in a vacuum over sulphuric acid, when glistening, pale yellow crystals were obtained. On submitting the solution to the usual Crum-Frankland and "urea" tests, a curious anomalous behaviour was noticed. The ratio of the total nitrogen to the nitrite nitrogen was found to vary in different preparations; thus, in one instance it was 2.43, in another 2.69, whilst in the third it was 3.4. If the substance were a pure nitrite, this ratio should invariably have been unity. At first these discrepancies led us to conclude that the substance obtained was a mixture of nitrate and nitrite in varying proportions; but, on the other hand, a strong base like piperazine would be expected to yield a stable nitrite. In one preparation it was noticed that crystals began to separate out after an interval of two hours; these were collected and dried with filter paper, and were found to be very sparingly soluble in water. The solution

on being shaken in the nitrometer with sulphuric acid gave nitric oxide, but on treatment with carbamide and dilute sulphuric acid no gas was liberated. Similarly, a solution of potassium iodide acidified with dilute sulphuric acid when placed in the nitrometer gave only a faint yellow tint, but no evolution of gas. The latter on being kept for some time began to deepen in colour owing to liberation of iodine, with evolution of nitric oxide, but the reaction was slow, and was only completed after an interval of several hours. It soon became evident that the first crop of crystals consisted, not of a nitrite at all, but simply of dinitrosopiperazine (m. p. 156°. Found, N=19.47. Calc., N=19.45 per cent.). The solution of this compound also proved to be practically a non-electrolyte; that it liberates iodine with evolution of nitric oxide on prolonged contact with the acidified solution of potassium iodide is, no doubt, due to its slowly undergoing hydrolysis. Peculiar interest, however, attaches to the fact that this dinitroso-compound gives up nitric oxide readily on being shaken with sulphuric acid in the nitrometer like an ordinary nitrate. A typical aliphatic nitroso-compound like nitrosodiethylamine does not, however, respond to this test. It thus became evident that the product obtained on evaporation to dryness in the earlier stages was a mixture of dinitrosopiperazine with the nitrite of the same base.

In view of the experiments described above, the following method was adopted for the isolation of pure nitrosopiperazinium nitrite. The solution obtained by double decomposition between piperazinium chloride and silver nitrite, which to start with gave the ratio of nitrogen by the Crum-Frankland and the "urea" method respectively as 2:1, was subjected to partial evaporation in a vacuum over sulphuric acid, and the successive crops which began to be deposited from day to day were separately collected. As a rule, the first two crops were found to be the pure dinitroso-compound—the third and fourth were more or less mixtures of the former with nitrosopiperazinium nitrite; at what particular stage the dinitroso-compound ceases to separate out depends on the concentration of the initial solution. If the concentration is hastened on the water-bath, dinitrosopiperazine is preferentially formed, and begins at once to crystallise out. Analyses of five distinct crops of as many preparations showed that the ratio nitrosic* to nitrite nitrogen was exactly unity. It might be urged that the substances that were obtained consisted of mixtures in well-nigh equivalent proportions of dinitrosopiperazine and piperazinium dinitrite, but

* As nitrosopiperazine gives nitric oxide, not like an ordinary nitrate, on treatment with sulphuric acid in a nitrometer, while the nitrosopiperazine, in respect to the "urea" test, the difference in molecular formula is almost negligible.

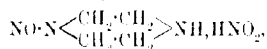
this is out of the question, as the former is very sparingly soluble, whilst the latter is very readily soluble in water. One hundred parts of water at 30° dissolve only 0.45 part of nitrosopiperazine; it can therefore scarcely be expected that even in the sixth crop the two compounds should persist in separating out in equal proportions. A complete analysis of the sixth crop gave the following result:

0.1304 gave 0.1504 CO_2 and 0.0772 H_2O . C = 31.39; H = 6.62.

0.0580 „ 18.4 c.c. N_2 (moist) at 28.4° and 760 mm. N = 34.67.
 $\text{C}_4\text{H}_9\text{ON}_3\cdot\text{HNO}_2$ requires C = 29.63; H = 6.17; N = 34.57 per cent.

If an alcoholic solution of piperazinium chloride is shaken with silver nitrite and the filtrate evaporated in a vacuum over sulphuric acid, the formula of the salt obtained approaches that of piperazinium dinitrite; thus in one preparation the ratio of total nitrogen by the Crum-Frankland method to that yielded by the "urea" method was 1.7/1.6 = 1.06. The yield was, however, very poor, as piperazinium chloride is only sparingly soluble in alcohol.

Nitrosopiperazinium nitrite,



is obtained in soft, green crystals; it is very readily soluble in water. The conductivity measurement at 25° is as follows:

Dilution.	Equivalent conductivity.	Dissociation per cent.
51	85.1	88.8
150	99.2	94.2
450	95.6	90.8

It will thus be seen that nitrosopiperazinium nitrite is ionised to the extent of about 89 per cent. at a dilution of 50 litres, and this might be expected from its behaviour as a nitrite of the ammonium type.

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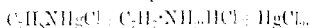
H.—Chlorides of the Mercurialkyl- and Mercurialkylaryl-ammonium Series and their Constitution as based on Conductivity Measurements.

By PRATULLA CHANDRA RÂY and NIBRATAN DHAR.

IN our previous investigation on the nitrites of the mercurialkyl- and mercurialkylaryl-ammonium series (T., 1912, 101, 687) we have noticed a striking analogy between these and the corresponding chlorides as described by Pesci (*Zetsch. anorg. Chem.*, 1897,

15, 225). It occurred to us that fresh light might be thrown on the vexed question of the constitution of the latter class of salts by a study of their conductivities, for which purpose they have been found to be sufficiently soluble in water. It will be shown below that our surmise has proved to be correct, and that the simplest formula is acceptable in every case, and that each and all of these compounds belong to the ammonium type of salts.

Pesci, for instance, describes mercuribenzyllammonium chloride as a "triple salt" with the complicated formula:



From the conductivity measurements it would appear that the simpler formula, $C_6H_5NH_2.HgCl_2$, is more appropriate, and that it yields the ions $(C_6H_5NH_2.HgCl)^+$ and Cl^- in aqueous solution.

Franklin, on the other hand, has been led to propose a different system of nomenclature (*J. Amer. Chem. Soc.*, 1907, **29**, 35; 1912, **47**, 3611). According to him, these compounds should be termed mercuric chloride with "amine, pyridine, and quinoline, etc., of crystallisation," or "ammonobasic mercuric chlorides."

EXPERIMENTAL.

Method of Preparation.—The composition of this class of salts varies considerably according to the method of preparation adopted. Pesci (*loc. cit.*) and André (*Compt. rend.*, 1891, **112**, 995) and others have often used cold or boiling aqueous or alcoholic solutions of mercuric chloride or of the amines. We rigidly adhered to a uniform method, consisting in adding an aqueous solution of the amine to a concentrated solution of mercuric chloride with continuous stirring until the ammoniacal odour became persistent.

As the presence of the minutest trace of amine hydrochloride formed during the reaction would seriously interfere with the conductivity measurements, the precipitate was in each case very carefully and repeatedly washed by the aid of the pump, and finally dried, as a rule, in the steam oven. It remains only to add that whereas mercuric nitrate invariably forms with amines, compounds of the "additive" type, mercuric chloride, on the other hand, yields, under similar conditions, compounds both of the "additive" and "substitutive" types; the latter tendency is very marked, probably owing to the fact that an atom of chlorine of mercuric chloride often combines with an atom of hydrogen of the amine to form hydrogen chloride. On account of wide divergence in their solubilities, no exact comparison is available, but a general idea may be easily obtained.

Since these compounds are sparingly soluble, and a minute quantity of impurity would seriously affect the accuracy of the results, very pure water is necessary; much precaution was therefore taken in purifying the water used for these conductivity measurements: its conductivity was 1.1×10^{-6} at 30° .

Mercuriammonium Chloride or Insoluble White Precipitate,
 NH_2HgCl .

The precaution necessary for the preparation of this substance in a state of purity has already been given in detail (*Zeitsch. anorg. Chem.*, 1902, **33**, 197). This compound has been included in the series, as it may be regarded as the parent substance from which the rest have been derived.

Mercurimethylammonium Chloride, $\text{NMe}(\text{H}_2\text{Cl})_2$.

This remarkable compound has not been described, as far as we are aware, by previous workers in this field. The equation of its formation, namely, $\text{NHMe}_2 + 2\text{H}_2\text{Cl} \rightarrow \text{NMe}(\text{H}_2\text{Cl})_2 + 2\text{HCl}$, should incline one to regard it as methylamine in which two atoms of hydrogen have been replaced by the two H_2Cl radicals. Its constitution will be discussed in the proper place.

Found: Hg = 81.73; Cl = 13.95; C = 2.00.

$\text{CH}_3\text{NCl}_2\text{Hg}$ requires Hg = 80.00; Cl = 14.20; C = 2.00 per cent.

It is worthy of note that under the ordinary conditions we have not succeeded in preparing ethyl and propyl substituted compounds of the present series.

Pesci, it is true, has described the ethyl derivative, NHEtH_2Cl ; but our attempts to prepare it ended in failure. The compound which was obtained by treating mercuric chloride with ethylamine gave Hg = 84.19, whilst NHEtH_2Cl requires Hg = 74.52 per cent. Propylamine yielded a dirty reddish-brown compound, which gave Hg = 84.88 per cent.

It is evident that in both these cases highly basic oxysalts were obtained, which enormously raised the percentage of mercury.

Mercuriisobutylammonium chloride, $\text{NH}(\text{C}_4\text{H}_9)_2\text{HgCl}$.

Found: Hg = 66.64. $\text{C}_4\text{H}_9\text{N}(\text{CH}_2)_2\text{Hg}$ requires Hg = 66.15 per cent.

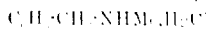
Mercuripiperazinium chloride, $\text{C}_4\text{H}_8\text{N}_2\text{H}_2\text{Cl}$.

Found: Hg = 62.38. $\text{C}_4\text{H}_8\text{N}_2\text{CH}_2\text{Hg}$ requires Hg = 62.30 per cent.

Mercuridimethylammonium chloride, $\text{CH}_3\text{CH}_2\text{N}(\text{HMe})_2\text{HgCl}$.

Found: Hg = 54.64. $\text{C}_2\text{H}_5\text{NCl}_2\text{Hg}$ requires Hg = 53.65 per cent.

Mercuridimethylammonium chloride,



Found: Hg=51.75; Cl=18.41. $C_8H_{11}NCl_2Hg$ requires Hg=51.02; Cl=18.11 per cent.

Mercuribenzylethylammonium chloride, $C_6H_5 \cdot CH_2 \cdot NH_2Et, HgCl_2$.

Found: Hg=49.76. $C_9H_{13}NCl_2Hg$ requires Hg=49.26 per cent.

Mercuriethylenediammonium chloride, $C_2H_4(NH_2)_2, 2HgCl_2$.

Found: Hg=67.25; Cl=23.56. $C_2H_6N_2Cl_4Hg_2$ requires Hg=66.44; Cl=23.58 per cent.

Mercuripyrindinium chloride, $C_5H_5N, 1\frac{1}{2}HgCl_2$.

Found: Hg=61.06. Theory requires Hg=61.89 per cent.

Mercuripicolinium chloride, $C_5H_4MeN, HgCl_2$.

Found: Hg=54.61. $C_6H_7NCl_2Hg$ requires Hg=54.94 per cent.

Mercurinicotinium chloride, $C_{10}H_{14}N_2, 1\frac{1}{2}HgCl_2$.

Found: Hg=50.88; Cl=19.95. Theory requires Hg=52.77; Cl=18.73 per cent.

Mercuripiperidinium chloride, $C_5H_{11}N, 2HgCl_2$.

Found: Hg=65.30; Cl=21.93. $C_5H_{11}NCl_4Hg_2$ requires Hg=63.79; Cl=22.4 per cent.

Mercurihexamethyltetrammonium chloride,
(CH_3)₆N₄, 2HgCl₂.

Found: Hg=57.94. $C_6H_{12}N_4Cl_4Hg_2$ requires Hg=58.65 per cent.

The piperidine compound is of a deep yellow colour, and is obtained by adding an aqueous solution of piperidine to mercuric chloride solution, and then diluting with water. The other members of this group are either colourless or pale yellow.

Mercuriammonium Chloride (Insoluble White Precipitate),
 NH_2HgCl .

Dilution.	Molecular conductivity.	Equivalent conductivity.	Equivalent conductivity.
950.02	42.018	41.501	210.24
1000.4	40.074	39.002	220.32
1800.8	48.008	40.004	240.34
5001.6	40.814	48.008	249.47

Mercuriethylenediammonium Chloride, $CH_2N(HgCl_2)$.

100.0	10.78	8.15	80.80
67.60	20.00	10.00	91.97
135.20	39.992	10.00	98.83
270.40	49.98	67.60	194.43

Mercuripiperidinium Chloride, $C_5H_{11}N, 2HgCl_2$.

100.0	202.30	101.15	60.72
33.33	177.00	91.50	68.83
8.33	185.00	92.50	71.25
167.20	410.70	410.00	78.37

Mercuriethylenediammonium Chloride, $\text{C}_2\text{H}_4(\text{NH}_2)_2\cdot 2\text{HgCl}_2$.

Dilution.	Molecular conductivity.	Dilution.	Equivalent conductivity.
1000	207.35	250	51.84
2000	222.32	500	55.58
4000	235.35	1000	58.84
8000	240.58	2000	60.14
16000	251.52	4000	62.83

Mercuriisramethylenetetrammonium Chloride, $(\text{CH}_2)_6\text{N}_4\cdot 2\text{HgCl}_2$.

578	109.32	1445	27.33
1156	132.73	2890	33.18
2312	145.42	5780	36.47
4624	150.35	11560	37.59
9248	155.08	23120	38.84

Mercuribenzylglythylammonium Chloride, $\text{C}_7\text{H}_7\cdot\text{NHEt}\cdot\text{H}_2\text{Cl}_2$.

3700	281.48	1850	142.24
7400	286.32	3700	143.16
14800	290.35	7400	145.17
29600	310.56	14800	155.18

Mercuribenzylmethyldiammonium Chloride, $\text{C}_7\text{H}_7\cdot\text{NHMe}\cdot\text{H}_2\text{Cl}_2$.

2735	269.47	10975	110.23
5470	273.58	21950	113.79
10940	275.18	43900	117.59
21880	280.42	87800	119.21

Mercuribenzylammonium Chloride, $\text{C}_7\text{H}_7\cdot\text{NH}_2\cdot\text{H}_2\text{Cl}_2$.

1080	• 150.20	5400	65.10
2160	216.00	10800	75.80
4320	230.32	21600	112.19
8640	236.64	43200	117.80
17280	248.56	86400	124.28

Mercurisobutylammonium Chloride, $\text{C}_4\text{H}_9\cdot\text{NH}\cdot\text{H}_2\text{Cl}_2$.

3675.0	35.32	150.00	47.00
3612.5	38.18	200.00	49.20
3625.0	109.56	4012.50	54.56
18125.0	120.05	9025.00	57.17

Mercuripiperazinium Chloride, $\text{C}_4\text{H}_9\text{N}_2\cdot\text{H}_2\text{Cl}_2$.

1131	125.66	16000	62.85
2262	130.32	32000	65.16
4524	137.56	64000	66.78
9048	137.38	128000	68.60
18096	139.58	256000	69.20

* The value of the molecular conductivity is given in the velocity of the ions, so that it is to be expected that its value would be different in different compounds. There is thus partial deviation from Werner's numbers.

Mercuripicolinium Chloride, C₅H₄NMe.HgCl₂.

Dilution.	Molecular conductivity.	Dilution.	Equivalent conductivity.
7280	1137.50	3640	568.75
14560	1150.35	7280	575.17
29120	1205.85	14560	602.92

Mercurypyridinium Chloride, 2C₅H₅N₂.3HgCl₂.

18206	1887.53	3641.2	314.59
36412	1892.33	6968.8	315.39
72824	1900.38	12137.6	318.39

Mercurinicotinium Chloride, 2C₁₀H₁₁N₂.3HgCl₂.

2520	420.00	420	70.00
5040	460.32	840	75.87
10080	520.36	1680	86.72
20160	560.56	3360	93.42

This compound evidently gives three chloridions (Cl') and a complex trivalent ion containing mercury.

Discussion of Results.

From the foregoing table it is evident that the molecular conductivities of some of the salts are about 100 at a dilution of 1000, whilst others have a value of about 250 at the same dilution, except infusible white precipitate, which is probably decomposed into simpler parts, namely, NH_4Cl and NH_3 (compare *Zeitsch. anorg. Chem.*, 1902, **33**, 205).

Adding to Werner's rule (Werner and Mielvi, *Zeitsch. physikal. Chem.*, 1893, **12**, 35; 1894, **14**, 506), it is probable that the former class of compounds yields two univalent ions in solution, whilst the latter, with an average of 250 as their molecular conductivity, yield three ions; the nicotine compound yields four ions, the value of its molecular conductivity being 450 at the same dilution. Mercurimethylammonium chloride appears to be of special interest. The two radicals, HgCl , are symmetrically disposed. It would, therefore, be reasonable to expect that the two chloridions (Cl') would behave similarly. The conductivity measurements actually bear this out. In solution the salt gives two chloridions (Cl') and one complex bivalent positive ion containing mercury. The result obtained in this case confirms Werner's rule. Although this compound was provisionally regarded as methyamine in which two atoms of hydrogen have been replaced by the radicle HgCl , in reality it is an ammonium derivative.

The pyridine and nicotine compounds are so very sparingly

soluble that no definite trustworthy conclusions can be drawn from their conductivity measurements.

In all these compounds mercury forms a part of a complex ion, so the ordinary tests for dimercurion (Hg^{++}) fail (for example, precipitation with hydroxidion (OH') or carbanion (CO_3^{--})).

Previous workers have designated these as additive compounds, but most probably they are not of this nature, as is evident from the considerations which have been already applied in the case of the corresponding nitrites (*loc. cit.*), namely:

(1) Ordinary tests for dimercurion (Hg^{++}) fail, so mercuric chloride cannot exist as such.

(2) The sum of molecular conductivities of the separate constituents is generally very much less than the actual conductivity of the salt (especially in the cases of piperazine, ethylenediamine, and benzylamine compounds).

(3) Tests for hydroxidion (OH') would be obtained if the amines are in the free state, as they yield hydroxidion in water; but the solutions give no such test. Moreover, the constituents (mercuric chlorides and amines) are easily soluble in water, whilst the salts formed from them are practically insoluble.

From the above arguments it is almost certain that these compounds are not of an additive nature, but are typical complex salts. In the case of the most soluble ones (for example, hexamethylenetetramine and pyridine compounds), silver chloride is precipitated when argention (Ag^+) is introduced into the solution; thus, chloridion (Cl') exists in the free state. So, in these compounds which yield only two ions the negative one is chloridion (Cl'), whilst the positive ion is a complex radicle containing mercury; for example, in hexamethylenetetrammonium mercuric chloride the two ions are $(\text{CH}_2)_6\text{N}_4\text{HgCl}'$ and Cl' respectively.

By the introduction of argention (Ag^+) silver chloride is deposited and equilibrium is disturbed, and the whole of the chlorine is precipitated.

Adopting Werner's idea in these compounds it is evident that one of the chlorine atoms are directly combined with mercury, and form a part of the complex ion (compare Jørgensen (*Zetsch. anorg. Chem.*, 1897, **14**, 446)). As in the other class of salts already studied (Rây, Dhar, and Dey), the direct linking is not quite as stable as those described by Werner (compare "New Ideas on Inorganic Chemistry," English Trans., pp. 32-43).

The mercurisulphine compounds studied by Hilditch and Smiles (*Cl.*, 1907, **91**, 59) are also complex compounds.

Silver compounds with the hydrogen as part of the complex positive ion have also been studied by Hellwig (*Zetsch. anorg.*

Chem., 1900, **25**, 187). Mercuric chloride and mercuric nitrite are feebly ionised, even at high dilutions. It is always seen that those electrolytes which are feebly ionised can easily form complexes (for example, mercuric iodide, mercuric cyanide, etc.). Abegg, in his "Theory of Electrolytic Dissociation" (English Trans., p. 117), has given a list of complex mercury compounds.

There is thus a distinct tendency in the case of mercury to form complex compounds.

From these arguments it is evident that the ammoniacal mercuric chlorides are typical complex salts with a tervalent, bivalent, or univalent complex radicle, containing mercury and the other part is always chloridion (Cl').

Thus, these bivalent salts behave like a simple chloride, such as barium chloride or zinc chloride, whilst the univalent salts are quite similar to chlorides, such as ammonium chloride or sodium chloride.

It will be seen that the present investigation and the previous one on the corresponding nitrites mutually strengthen and confirm each other.

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III.—*Equivalent Conductivity and Ionisation of Nitrites.*

By PRAFULLA CHANDRA RÂY and NILEATAN DHAR.

THE study of nitrites from the point of view of equivalent conductivity and ionisation was undertaken by Pick (*Diss.*, Breslau, 1906) but he worked only with a very limited number of salts. Ley and Kissel (*Ber.*, 1899, **32**, 1363) measured the equivalent conductivity of mercuric nitrite alone. Rây and Mukherjee (*P.*, 1910, **26**, 173) studied the ionisation of a series of alkali nitrites from their cryoscopic behaviour. In our study of the nature of the complexes of potassium mercurinitrite we have incidentally measured the equivalent conductivities of mercuric nitrite, potassium nitrite, and potassium mercurinitrite (*T.*, 1912, **101**, 965). With the view of throwing light on the constitution of this important group of salts, an exhaustive study of their equivalent conductivities and ionic behaviour has been undertaken. As a rule, crystals of these

nitrites were prepared, and freed from adhering mother liquor. Generally, these salts were obtained by double decomposition between silver nitrite and the corresponding chloride and evaporation in a vacuum of the filtrate. Evaporation on the water-bath had to be avoided, as these nitrites undergo marked hydrolysis at high temperatures. The nitrites of the alkylammonium bases which have been included in this paper are those recently described by Ráy and Rakshit (T., 1911, **99**, 1470; 1912, **101**, 141, 216). Sometimes, also, salts in solution only were obtained by double decomposition between barium nitrite and equivalent proportion of the corresponding sulphate in a tall cylinder (compare Ráy and Dhar, *loc. cit.*). This procedure was necessary for those nitrites the solutions of which decompose when their concentrations are increased (for example, copper and nickel nitrites). The temperature was $20^{\circ} \pm 0.1^{\circ}$.

The water used in these measurements was purified by continuous distillation with a tin condenser, first by means of acid permanganate, and then of alkaline permanganate; all the joints also were of tin. This arrangement was that of Jones and Markay (*Zeitsch. physikal. Chem.*, 1894, **14**, 317) with a few alterations. The conductivity of the water used was 1×10^{-6} at 20° .

In the following tables the value of the maximum equivalent conductivity is obtained by adding the separate ionic mobilities of the cation and anion, since the maximum equivalent conductivity cannot be exactly obtained by ordinary measurements, the values being sometimes highly affected by hydrolysis.

The values of ionic mobility for the univalent ions at 18° are primarily based on Kohlrausch's figures. The small changes are due to the use of 0.436, instead of 0.497, for the cation transference number of potassium chloride and to the change of atomic weight adopted in 1911. The corrections for temperature were made by Kohlrausch's equation:

$$(\Delta K_1) = \frac{1}{K_{18}} \times \frac{K_1 - K_{18}}{t - 18},$$

where K_1 and K_{18} are the conductivities at the temperatures t , 18° ; ΔK_1 is the temperature coefficient which gives the change of conductivity expressed as a function of conductivity, K_{18} , at 18° for a change in the temperature of 1° .

Also the following equation of Kohlrausch can be very advantageously used in obtaining the migration velocity of an ion at temperatures not far removed from 18° :

$$U_1 = U_{18} \times \{1 + \alpha(t - 18) + \beta(t - 18)^2\}.$$

The values for α and β are taken from Kohlrausch's tables (*Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1031).

The ionic mobility of nitrosion (NO_2^-) at $25^\circ = 61.7$ (Vogel *Zeitsch. anorg. Chem.*, 1903, **35**, 403), whilst Pick (*loc. cit.*) give it as 63 at 25° and 57 at 18° . The latter values are probably a little too high, since he has taken the equivalent conductivity of silver nitrite at a molar concentration of $0.0265 = 69.4$, the value which is actually found. This value is, however, higher than the actual value owing to hydrolysis.

Ammonium Nitrite.

Crystals of ammonium nitrite sublimed in a vacuum were used in this experiment (compare Rây, Dhar, and Dey., T., 1912, **101**, 1185).

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
20.7	96.72	180.3	107.69
62.1	104.54	558.9	110.22

The calculated value of λ_{∞} for ammonium nitrite at 20° is 126.3.

Lithium Nitrite.

Crystals of this salt were used in this measurement.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
6	79.32	132	100.00
18	75.00	486	102.05
54	91.52		

The calculated value of λ_{∞} for lithium nitrite at 20° is 93.7.

Sodium Nitrite.

Crystals were used.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
9	78.98	243	109.55
27	94.40	729	119.50
81	103.65		

The calculated value of λ_{∞} for sodium nitrite at 20° is 104.5.

Calcium Nitrite.

Crystals of this salt were used.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
5.8	70.00	156.6	108.75
17.4	96.66	469.8	110.26
52.2	103.57		

The calculated value of λ_{∞} for calcium nitrite at 20° is 112.9.

Strontium Nitrite.

Crystals were used.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
12	85.55	324	129.60
36	92.30	972	124.91
108	111.11		

The calculated value of λ_{∞} for strontium nitrite at 20° is 113.

Barium Nitrite.

Crystals were used.

Dilution	Equivalent conductivity.	Dilution.	Equivalent conductivity.
6.31	78.88	179.37	122.38
18.93	97.56	541.11	124.14
56.79	111.61		

The calculated value of λ_{∞} for barium nitrite at 20° is 116.75.

Disturbances due to hydrolysis are very marked in this case.

Magnesium Nitrite.

The conductivity experiment was made with solution.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
15.5	91.15	132.5	124.55
46.5	108.65	448.5	127.15

The calculated value of λ_{∞} for magnesium nitrite at 20° is 106.9

Zinc Nitrite (in Solution).

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
124	59.27	348	116.24
372	89.87	1044	117.67
1116	104.00		

The calculated value of λ_{∞} for zinc nitrite at 20° is 108.1.

This solution is very feebly acid. This is due to the hydrolysis of the salt.

Silver Nitrite.

Crystals (purified by recrystallisation) were used.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
79.6	79.32	6484	115.62
2318	85.75		

The calculated value of λ_{∞} for silver nitrite at 20° is 115.2.

Tetramethylammonium Nitrite.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
20.4	83.52	163.2	103.83
40.8	95.51	326.4	106.53
81.6	101.12	652.8	109.65

The calculated value of λ_{∞} for tetramethylammonium nitrite at 20° is 99.2.

Phenyldimethylethylammonium Nitrite.

Crystals were used.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
29.6	72.11	691.2	92.21
76.8	82.82	2073.6	93.80
230.4	87.63	6220.8	94.20

The calculated value of λ_{∞} for phenyldimethylammonium nitrite at 20° is 85.4. This salt is feebly alkaline to litmus.

isobutylammonium Nitrite.

Crystals were used.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
28	75.55	252	81.12
84	80.35	756	81.92

The calculated value of λ_{∞} for isobutylammonium nitrite at 20° is 91.3.

The solution is almost neutral to litmus.

Butylammonium Nitrite.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
16	67.61	328	75.23
32	69.60	656	81.10
64	67.85	312	80.50

The calculated value of λ_{∞} for butylammonium nitrite at 20° is 91.3.

The solution is feebly alkaline to litmus.

Allylammmonium Nitrite.

Viscous liquid was used.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
17.8	79.46	169.2	96.50
53.4	87.12	486.6	192.25

The calculated value of λ_{∞} for allylammmonium nitrite at 29° is 91.

The solution reacts feebly acid.

Dipropylammmonium Nitrite.

Crystals were used.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
24	69.55	216	84.44
72	79.15	648	85.02

The calculated value of λ_{∞} for dipropylammmonium nitrite at 29° is 82.9.

The solution reacts very feebly alkaline.

Propylammmonium Nitrite.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
14	71.27	136.8	95.52
212	80.1	369.4	111.7
636	92.81		

The calculated value of λ_{∞} for propylammmonium nitrite at 29° is 94.

The solution reacts very feebly acid.

Tripropylammmonium Nitrite.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
7.4	66.66	189.6	76.85
63.1	73.65	467.6	96.89

The calculated value of λ_{∞} for tripropylammmonium nitrite at 29° is 78.2.

The solution is almost neutral to litmus.

Diethylammonium Nitrite.

Crystals were used.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
23.3	81.55	209.7	95.53
69.9	96.25	629.1	100.32

The calculated value of λ_{∞} for diethylammonium nitrite at 20° is 88.7.

The solution reacts very feebly alkaline.

Triethylammonium Nitrite.

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
60	85.52	540	91.25
180	89.21		

The calculated value of λ_{∞} for triethylammonium nitrite at 20° is 105.2.

The solution is almost neutral to litmus.

Nickel Nitrite (in Solution).

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
18.17	57.32	163.53	95.35
54.51	78.52	499.59	114.12

The calculated value of λ_{∞} for nickel nitrite at 20° is 94.0.

The solution is feebly acid to litmus.

Copper Nitrite (in Solution).

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
18.12	58.55	162.58	96.46
54.36	79.22	487.74	111.18

The calculated value of λ_{∞} for copper nitrite at 20° is 106.8.

The solution is feebly acid.

Sodium Mercurinitrite.

(Rây, T., 1907, **91**, 2631.)

Dilution.	Equivalent conductivity.	Dilution.	Equivalent conductivity.
199	226.35	399	266.72
399	250.69		

Like its potassium analogue (*loc. cit.*), in concentrated solutions only this salt behaves as a complex salt with the ions Na^+ and mercurinitrosion, $\text{Hg}(\text{NO}_2)_4^{2-}$; but as it is diluted it begins to decompose into its constituents, as is seen in the table; thus at a dilution of about 1000, the equivalent conductivity is nearly 265, showing that this salt behaves like a salt decomposing into three ions (compare Werner and Miolati, *Zeitsch. physikal. Chem.*, 1893, **12**, 35; 1894, **14**, 506). At higher dilutions the value of the equivalent conductivity increases very fast owing to decomposition.

The solution has a slightly acid reaction due to hydrolysis of mercuric nitrite, which more than counterbalances the alkalinity due to the hydrolysis of sodium nitrite.

Tetramethylammonium Mercurinitrite.

Crystals were used.

Dilution.	Equivalent conductivity at 20°.	Dilution.	Equivalent conductivity at 20°.
76	191.60	6.4	120.31
228	115.72		

Similarly, this salt behaves in a concentrated solution like a complex salt. On dilution it begins to decompose, and the equivalent conductivity attains the value of about 150 instead of nearly 100 at a dilution of 1000 (compare Werner and Miolati, *loc. cit.*). It shows slight acidity, due to the same reason as in the previous salt.

Mercurousmercuric Nitrite, $2\text{Hg}(\text{NO}_2)_2 \cdot \text{Hg}_2(\text{NO}_2)_2$ (solid body).

Dilution	Equivalent conductivity at 20°.
187	62.60
561	80.10

The preparation of this salt has been described by one of us (*ibid.*, T., 1902, **81**, 645). It behaves like a univalent salt, giving only two ions in solution; thus the equivalent conductivity at a dilution of about 1000 litres is nearly 100. At very high dilutions the salt, like other complex salts, begins to dissociate into simpler parts.

In this salt the ions are mercurousion (Hg^+) and the univalent complex ion dimercurinitrosion, $\text{Hg}_2(\text{NO}_2)_2^-$. At very high dilutions the complex begins to decompose, and causes acidity due to the hydrolysis of mercuric nitrite which is formed.

* This salt exists only in solution; on evaporation it is converted into the nitrate.

Discussion of Results.

The equivalent conductivities of the nitrites, as is evident from the foregoing tables, do not reach a maximum value since they undergo hydrolysis. In the alkali and alkaline earth nitrites, a weakly basic reaction is obtained, since the corresponding hydroxides are strong bases; whilst in the case of copper, zinc, nickel, mercury nitrites, etc., there is a feebly acid reaction since the hydroxides are very feeble bases, and this indirectly proves also that nitrous acid is not a very weak acid, thus corroborating the evidence of Schumann (*Ber.*, 1900, **33**, 1527) and Blanchard (*Zeitsch. physikal. Chem.*, 1902, **41**, 681).

In the case of the alkylammonium nitrites the behaviour would also depend on the strength of the amines (compare Bredig, *Zeitsch. physikal. Chem.*, 1894, **13**, 191).

In the compounds studied by us, effects due to hydrolysis must be reckoned with, for on account of the high velocities of hydron and hydroxidion, the value of λ_{∞} is seriously affected, even if the degree of hydrolysis is very small. The hydrolysis in the case of calcium nitrite is rendered evident from the milkiness of the solution when evaporated on a water bath. In the case of strontium nitrite it is much more marked; in fact, a pellicle of strontium carbonate is formed on the surface, and the solution is found to be more and more alkaline. Pick also noticed the turbidity of calcium nitrite solution, but has overlooked the real cause of it (*loc. cit.*, p. 16). Hence the value of the equivalent conductivity of the nitrates as measured by Kohlrausch, Noyes, and Jacobsen is a little lower than the corresponding nitrites at a similar dilution, although the ionic mobility of nitration is almost equal to that of nitrosion.

It is evident from this work that the amine nitrites behave like typical ionogens, and are similar to alkali and alkaline earth nitrites.

It will also be seen that the results arrived at by the conductivity measurements corroborate in the main those deduced from the cryoscopic method by Rây and Mukherjee.

We are now engaged in measuring the viscosity and the degree of hydrolysis of the nitrites, so that the true degree of dissociation of these salts may be ascertained.

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IV.—*Viscosity and Association. Part III. The Existence of Racemic Compounds in the Liquid State.*

By FERDINAND BERNARD THOLE.

THE question of the existence of liquid racemates is one that has received considerable attention during the past twenty years, and in few such problems have the experimental data and resulting deductions been more contradictory.

Such a result is somewhat to be expected, for the conclusions, in practically every case, have been based on the study of physical properties and constants, and few of these are sufficiently constitutive or accurate to give figures the interpretation of which is not open to doubt, especially as liquid racemates, if they do exist, are probably dissociated to a great extent into their components.

In two previous papers (T., 1908, **93**, 1815; 1910, **97**, 1249), the author attempted to solve the problem by determining the viscosities of active and inactive isomerides, since viscosity is undoubtedly one of the most valuable constitutive properties, and, moreover, is one which gives very accurate results with a limited quantity of material. The results showed that racemic compounds can exist in solution, although in most cases the racemate on solution dissociates either completely or to a very considerable extent into the mixture of dextro- and laevo-forms.

The following is a summary of the chief resources that have been published on this question:

Colour. Byk has shown (*Zeitsch. physikal. Chem.*, 1904, **49**, 482) that solutions of copper tartrate and copper racemate differ in colour, the former being blue and the latter greenish-blue.

Molecular Volume. Murchewski found that tartaric acid in aqueous solution has a smaller specific volume than racemic acid. La Ranken and Taylor have pointed out (*Proc. Roy. Soc. Edin.*, 1907, **27**, 172) that these results, which agree with those of Perkin (T., 1887, **51**, 362), require confirmation.

Molecular Weight. Anschütz and Kienitz, who first determined the molecular weights of active and racemic dimethyl diacetyl tartrate by the cryoscopic method, obtained no evidence of racemic complexes in solutions. Bruni and his co-workers (*Atti R. Accad. Lincei*, 1902, [v], **11**, 212; 1904, [v], **13**, 319) have more recently shown that whilst this result is true for dilute solutions, dissociation is only partial in more concentrated solutions in the case of dimethyl racemate, dimethyl diacetyl racemate, ammonium hydrogen tartrate, and ethyl *dl* dibromophenylpropionate.

Affinity Constant. According to Ostwald (*Zeitsch. physikal. Chem.*, 1889, **3**, 372), active and inactive tartaric acids have the same conductivity.

Temperature Effects.—Pasteur and Ladenburg have shown that when certain dextro- and levo-isomerides (*d*- and *l*-tartaric acids and *d*- and *l*-coniine) are mixed in the liquid condition heat is evolved, but Adriani (*Zeitsch. physikal. Chem.*, 1900, **33**, 453) does not accept this as evidence of racemate formation.

Freezing-point Curves. A great deal of work has been done in this connexion on the lines laid down by Roozeboom (*Zeitsch. physikal. Chem.*, 1899, **28**, 494), the chief workers in this field being Adriani, who obtained curves consisting of two eutectics and one maximum at 50 per cent. in the cases of dimethyl tartrate, dimethyl diacetyltartrate, mandelic acid, and benzoyltetrahydroquinoline, and Findlay and Hickmans (T., 1907, **91**, 905), who obtained similar curves with the *l*-menthyl mandelates. The latter authors have confirmed their conclusions by a series of solubility measurements (T., 1909, **96**, 1386). Kipping considers that racemic compounds may have a free existence in the liquid state, since *d*-hydrindamine *dl*-mandelate is resolvable by crystallisation from water, whilst *dl*-hydrindamine *d*-mandelate could not be so resolved (T., 1909, **95**, 465, 1386).

Absorption Spectra. Stewart (T., 1907, **91**, 1337) determined the absorption spectra of aqueous solutions of dextro-, meso-, and racemic tartaric acids, and found that the absorption curve of the last-named acid began to diverge from that of the other forms at concentrations above 14 per cent.

Viscosity.—Ranken and Taylor have pointed out that in moderately concentrated solutions racemic acid has a lower viscosity than tartaric acid.

Beck (*Zeitsch. physikal. Chem.*, 1901, **48**, 670) has determined the viscosities of a number of active and inactive compounds in the fused state. In the cases of camphoroxime and carboxime the methods agree that the inactive substance is a $\frac{1}{2}$ racemic mixture and not a true racemate. In the cases of dimethyl racemate and dimethyl diacetylracemate, freezing-point curves and cryoscopic measurements show the free existence of the racemic compound.

Beck states, however, that his viscosity results show no indication of a liquid racemate in any of the above-mentioned substances.

In two previous papers (T., 1908, **93**, 1-15; 1910, **97**, 1219) the author investigated the viscosities of a number of active and inactive compounds in solution. In some cases the results must be taken with some reserve, owing to the difficulty of careful purification without inducing racemisation.

Definite evidence was, however, obtained that racemic acid can exist to a limited extent in aqueous solution, the dissociation being, however, nearly complete at low concentration. The dextro- and inactive octyl hydrogen phthalates in benzene solution possess identical viscosities, as do the mandelic acids in water and pyridine solutions. In the case of the mandelic acids in amyl acetate solution there appears to be a slight divergence of the viscosity-concentration curves for solutions of the active and inactive acids.

The differences are, however, very small, and, as was emphasised in the paper, the evidence afforded was merely suggestive, and not conclusive, of the existence of racemic mandelic acid in the solution.

From the above results the following conclusions may be fairly drawn:

(1) Although racemic compounds undoubtedly exist in many cases in the solid state, the evidence for their existence in solution or in the fused state is conflicting.

(2) The majority of the evidence seems to point to the limited existence of liquid racemate complexes, although dissociation takes place to a very considerable extent when a racemate passes into the liquid condition.

(3) In dilute solutions all the results show complete dissociation, and only in the case of more concentrated solutions is any evidence found of racemate existence; moreover, the degree of dissociation at a given concentration and the rate of dissociation with dilution depend on the nature of the solute and the solvent. In fact, the position appears precisely analogous to that of the electrolytic dissociation of salts in dilute solution, and is on a par with that of the existence of double salts in solution.

Through the kindness of Dr. Pickard and Mr. Kenyon a number of active and inactive alcohols have been placed at the author's disposal, and an opportunity has been thus afforded for extending considerably the previous viscosity determinations in connexion with this subject. At the same time, owing to very considerable improvements in the apparatus used, it has been possible to extend the measurements to a considerably wider range of substances.

EXPERIMENTAL.

The manipulative difficulties involved in the determination of viscosities of the substances detailed below were considerably increased by the limited quantity of material and by the necessity for investigating in the fused state certain compounds which are solid at the ordinary temperature. It was necessary, therefore, to design a viscometer which should be capable of giving fairly accurate

results with not more than 1 c.c. of liquid, and at the same time obviate the difficulty and waste of filtering fused solids into the apparatus (a precaution quite necessary with the older forms of viscometer).

The type of instrument used is figured below, and while based essentially on the Ostwald principle is provided with a horizontal capillary and with two small wells or sumps into which particles of foreign matter may settle.

The smaller instrument (Fig. 1) was used in the investigation of the active alcohols, and had a capacity of 0.7 c.c. The receiving limb was made of glass tubing of 3 cm. bore, and had a bulb of

FIG. 1.

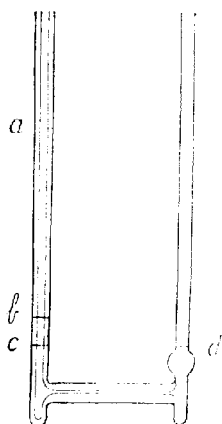
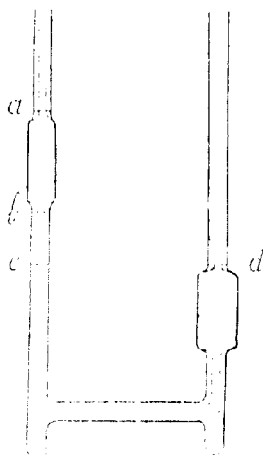


FIG. 2.



about 0.3 c.c. capacity near its lower end. The horizontal capillary was 5 cm. long and 0.03 cm. bore, and the measuring limb 20 cm. long and 0.2 cm. bore. The viscometer was suspended vertically in the thermostat, and filled with liquid until the meniscus registered with the etched lines *ab*, any excess being removed with a capillary pipette. Twenty minutes were allowed for complete drainage from the sides of the receiving limb, and the levels were then finally adjusted. The liquid was then drawn above the etched line *a*, and the time of flow of the upper meniscus from *a* to *b* noted, a lens being used to give increased accuracy in timing. The experimental results show that even on such a small scale consistent values can be obtained.

The average error is indicated by the following typical results with viscometers of the smaller type (0.7 c.c. capacity).

Viscometer A.—l-Heptan- β -ol.

Time of flow in seconds.

	213.4	
	214.2	
	214.4	Mean = 214.0.
	214.0	
Viscometer A	<i>l</i> -heptan- β -ol.....	Viscosity..... 0.65055
"	<i>U</i> <i>d</i> -heptan- β -ol.....	0.65012
"	<i>A</i> <i>d</i> - <i>n</i> -butylisopropylcarbinol...	0.65683
"	<i>U</i> <i>d</i> - <i>i</i> -butylisopropylcarbinol...	0.65779
		Density..... 0.8155
		0.8155
		0.8210
		0.8212

In all the other cases sufficient material was available to permit the use of the larger apparatus (Fig. 2), which had a capacity of 24 c.c., and has now been adopted as the standard type of instrument in the present series of researches. For use with volatile or hygroscopic substances guard tubes of the type described in a previous paper (T., 1910, **97**, 2598) may be ground to the open ends of the limbs.

The viscometers were calibrated with ethylene dibromide, and in certain cases with aniline, liquids which are particularly suitable, as they can be readily obtained in a high state of purity.

The specific gravities at 25° were determined in Sprengel pycnometers, and at the higher temperatures in a small bulb of 3 c.c. capacity.

In the experiments at 25° the temperature of the bath was maintained within 0.01° by means of a Lowry spiral thermometer. For the higher temperatures a large beaker of water was used, the heating being controlled by hand, and the temperature maintained within 0.1°. Control of the temperature was greatly facilitated by covering the water with a film of mineral oil, which prevented rapid evaporation.

The octyl hydrogen phthalates were prepared from *sec*-octyl alcohol by the method described by Pickard and Kenyon (T., 1907, **91**, 2058).

The menthyl mandelates were prepared from the acids and menthyl by the Fischer-Speier methods described by McKenzie and Finlay and Hickmans respectively (T., 1904, **85**, 42, 43, 1907, **91**, 965).

The esters of tartaric and mandelic acids were purified by repeated fractional distillation under diminished pressure, care being taken to prevent the absorption of moisture by these substances (compare Beck, *Z. physikal. Chem.*, 1904, **48**, 670).

The *d*- and *l*-carvoximes were purified by crystallization, and the

inactive oxime was prepared by melting together equal weights of the isomerides.

The alcohols were lent by Dr. Pickard and Mr. Kenyon, and used without further purification.

TABLE I.
The Octyl Hydrogen Phthalates.

<i>Dextro.</i>		<i>Inactive.</i>	
Temperature.	Time of flow (in seconds).	Temperature.	Time of flow (in seconds).
65°	151.6	65°	153.9
71	113.6	70	120.1
76	90.2	75	94.0
80	77.4	80	77.5
85	63.5	85	63.4

Owing to lack of material, accurate density-determinations could not be made, and therefore times of flow were measured over a temperature range. The results when plotted are found to lie on a single curve, showing that no racemic compound is present.

This conclusion was previously arrived at from the viscosities of benzene solutions of these esters.

TABLE II.
The ac-Tetrahydronaphthols.

<i>Dextro.</i>		<i>Inactive.</i>	
Temperature.	Time of flow (in seconds).	Temperature.	Time of flow (in seconds).
34°	231.3	31.1°	296.4
40	141.7	38.0	165.0
48	81.7	44.0	106.0
55	54.0	50.0	71.6
		55.0	53.4
		62.4	36.7

In this case also the results lie on a single curve, showing the absence of any racemate in the inactive mixture.

TABLE III.
The Alcohols at 25°.

Alcohol.	Viscosity.			
	<i>d.</i>	<i>l.</i>	<i>dl</i> (found).	<i>dl</i> (calculated).
Phenylethylcarbinol ...	0.1393	0.1306	0.1349	0.1344
Heptan- β -ol	0.05042	0.05055	0.05055	0.05048
Octan- β -ol	0.06328	0.06550	0.06490	0.06460

In the case of octan- β ol the value in the third column is that of a mixture containing 60 per cent. of the dextro-form, and the

viscosity value in column 4 is calculated for a mixture of this composition.

The results in the last two columns indicate clearly that the inactive mixture is only a conglomerate.

TABLE IV.
The Carvoximes.

Fused at 95°.		In amyl acetate solution at 25° (1 gram of oxime in 7 c.c. of solvent)	
	Viscosity.		Viscosity.
Dextro	0.0476	Dextro	0.01109
Inactive	0.0474	Inactive	0.01111

Since the active forms of this oxime melt at 73° and the mixture at 92°, this might be expected at first sight to be a genuine case of the existence of a racemate. Adriani has, however, shown that the freezing-point curve exhibits a maximum at 50 per cent., but no eutectics. In other words, the substance melting at 92° consists of ψ -racemic mixed crystals, and is not a genuine racemic compound. This conclusion is amply confirmed by the viscosity results, both in the fused state and in solution. Beck has also determined the viscosities of various mixtures of *d*- and *l*-carvoximes, and his results are in full agreement with those detailed above.

TABLE V.
The Tartaric Esters.

Ester.	Temperature.	Viscosity.
Methyl <i>d</i> -tartrate	85°	0.133
" racemate	85	0.130
" " + methyl tartrate (50 per cent.)	85	0.131
Ethyl <i>d</i> -tartrate	25	1.457
" racemate	25	1.360

The esters of tartaric acid (particularly the ethyl esters) are notably difficult to purify, especially in view of their hygroscopic nature.

In the cases investigated, therefore, repeated vacuum distillation was employed until approximately constant viscosity-values were obtained.

In the case of dimethyl racemate several methods, notably freezing-point curves and cryoscopic measurements, seem to indicate that this substance is capable of actual existence. The ester was investigated by Beck, who determined the viscosities of a range of mixtures of the dextro- and inactive esters. He concluded that his results were in sufficient agreement to preclude the possibility of

the existence of a racemate. When plotted, however, they lie on by no means a smooth curve, and must be accepted with some reserve. The viscosities detailed above seem to indicate the probable existence to an appreciable extent of both dimethyl and diethyl racemates in the liquid state, the racemate, as in the case of the free acid, possessing a lower viscosity than the active form.

Beck further investigated the viscosities of fused dimethyl diacetyltartrate and dimethyl diacetylracemate, and concluded that the two esters had the same viscosity, showing the absence of any racemic compound. His results are appended, and it will be noticed that they are capable of another interpretation, since with one exception the viscosity falls with increasing concentration of the inactive ester.

TABLE VI.

Dimethyl Diacetyltartrate and Diacetylracemate at 104° (Beck).

Mixture.	Viscosity (η of water at 25° = 1).
Pure racemate	6.764
{ 90 per cent. racemate	6.666
{ 10 " active ester	
{ 60 " racemate	6.912
{ 40 " active ester	
Pure active ester	6.933

Bruni has proved by cryoscopic measurements that dimethyl diacetylracemate can exist in non-dissociating solvents, such as ethylene dibromide, and Adriani's freezing-point curve shows two eutectics and a maximum at 50 per cent. of each active form.

TABLE VII.

The 1-Menthyl Mandelates.

<i>In amyl acetate solution at 25°</i>		
<i>Fus'd at 85°. (1.1 gram of ester in 7 c.c. of solvent).</i>		
	Viscosity.	Viscosity.
1-Menthyl <i>dl</i> -mandelate ...	0.0653	0.01110
" <i>l</i> -mandelate ...	0.0632	0.01085

These esters have been fully investigated by Findlay and Hickmans, who conclude from freezing point curves and solubility determinations that the partly racemic ester is capable of free existence.

This conclusion is fully borne out by the above viscosity results.

TABLE VIII.

The Ethyl Mandelates at 25°.

Ester.	Viscosity.
Ethyl <i>dl</i> -mandelate	0.1971
" <i>l</i> -mandelate	0.1971

These results demonstrate clearly that ethyl *dl*-mandelate is completely dissociated under the conditions of the determinations.

Summary of Results.

(1) In most cases *dl*-liquids and solutions are merely conglomerates. This has been shown in the cases of octyl hydrogen phthalate, *tc*-tetrahydronaphthol, phenylethylcarbinol, heptan- β -ol, octan- β -ol, parvoxime, and ethyl mandelate.

In certain instances proof has been afforded by viscosity, and in some cases confirmed by other physical methods, of the existence in solution and in the fused state of racemic complexes.

The cases investigated in the present research were methyl and ethyl racemates and *l*-menthyl *r*-mandelate. It is perhaps worthy of mention that nearly all the definitely established liquid racemates are derivatives of the hydroxy-carboxylic acids.

(2) In the cases where racemate existence in solution has been substantiated, dissociation is very considerable, even at fairly high concentrations in a comparatively non-dissociating solvent.

The author desires to express his thanks to Dr. Pickard and Mr. Kenyon for the loan of material, and to the Research Fund Committee of the Chemical Society for a grant which has partly covered the expenses entailed.

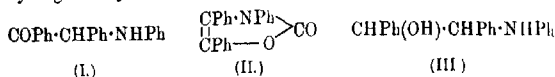
EAST LONDON COLLEGE.

V. — *The Formation of Tetrahydro-oxazoles from α -Hydroxy- β -anilino- $\alpha\beta$ -diphenylethane and its Homologues.*

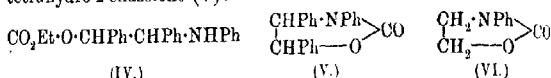
By HORACE LESLIE CROWTHER and HAMILTON McCOMBIE.

It has been shown by McCombie and Parkes (T., 1912, 101, 1991) that α -keto- β -anilino- $\alpha\beta$ -diphenylethane (I), when condensed with carbonyl chloride in toluene solution, yields 3:4:5-triphenyl-2:3-dihydro-2-oxazolone (II). It was found impossible, however, to convert this dihydro-oxazolone into a tetrahydro-oxazolone by the action of reducing agents, as the compound was either recovered unchanged or converted into dibenzyl, with complete destruction of the oxazole ring. In this respect the oxazole ring behaves very

similarly to the glyoxaline ring, which it is found impossible to hydrogenise by the direct action of reducing agents:



Attempts have been made by the authors to obtain tetrahydro-oxazolones from α -keto- β -anilino- $\alpha\beta$ -diphenylethane by first reducing that compound to α -hydroxy- β -anilino- $\alpha\beta$ -diphenylethane (III), employing the method described by Voigt (*J. pr. Chem.*, 1886, [ii], 34, 9), forming the ethylcarbonato-derivative (IV), and eliminating alcohol according to the method described by McCombie and Parkes (*loc. cit.*). This method, however, resulted merely in the regeneration of the original hydroxy-compound. A successful synthesis of tetrahydro-oxazolones was attained by the direct condensation of α -hydroxy- β -anilino- $\alpha\beta$ -diphenylethane (III) with carbonyl chloride in toluene solution, when there resulted 3:4:5-triphenyl-2:3:4:5-tetrahydro-2-oxazolone (V):



By similar condensations the corresponding *m*- and *p*-tolyl and β -naphthyl derivatives were obtained, in which these substituents are attached to the nitrogen atom. It was found impossible to prepare the *o*-tolyl analogue because the conditions necessary for the reduction of α -keto- β -*o*-toluidino- $\alpha\beta$ -diphenylethane to the corresponding hydroxy-compound could not be discovered.

The tetrahydro-oxazolones described in this communication are closely related to 3-phenyl-2:3:4:5-tetrahydro-2-oxazolone (VI), which is described by Nemirowski (*J. pr. Chem.*, 1885, [ii], 31, 175) and by Otto (*ibid.*, 1891, [ii], 44, 17).

These tetrahydro-oxazolones were found to be very stable substances. They were not reduced by sodium amalgam, or even by sodium in amyl-alcoholic solution. Phosphorus trichloride was without action on them, and their basicity was so slight that no hydrochloride or picrate could be isolated.

It was thought possible that compounds similar to the sulphazoles described by McCombie and Parkes (*loc. cit.*) might be prepared from these hydroxy-compounds by substituting thionyl chloride for carbonyl chloride in the reaction described above. In the case of the aniline compound a very small quantity of a condensation product was obtained. In the case of the other compounds, no trace of a condensation product could be isolated, so that evidently there is little or no tendency for thionyl chloride to yield cyclic compounds with these hydroxy-derivatives. Similar

negative results were obtained when sulphuryl chloride was substituted for carbonyl chloride.

EXPERIMENTAL.

α -Ethylcarbonato- β -anilino- $\alpha\beta$ -diphenylethane, $C_{23}H_{26}O_3N$.

This compound was obtained by dissolving the base in dimethylaniline and adding excess of ethyl chlorocarbonate. The mixture was allowed to remain in the cold for twelve hours, and was then poured into dilute hydrochloric acid. The carbethoxy-compound separated as a viscid mass, which, when recrystallised from dilute alcohol or light petroleum, melted at 114° :

0.2000 gave 7.2 c.c. N_2 at 14° and 739 mm. $N=4.07$.

$C_{23}H_{26}O_3N$ requires $N=3.88$ per cent.

This carbethoxy-compound, on treatment with alcoholic potassium hydroxide, gave *α -hydroxy- β -anilino- $\alpha\beta$ -diphenylethane*.

3:4:5-Triphenyl-2:3:4:5-tetrahydro-2-oxazolone, $C_{21}H_{17}O_2N$.

This substance was obtained by dissolving 2 grams of *α -hydroxy- β -anilino- $\alpha\beta$ -diphenylethane* in 25 c.c. of dry toluene, and adding 8 grams of carbonyl chloride in toluene (20 per cent. solution). The mixture was allowed to remain overnight, when a white product separated. The excess of carbonyl chloride was removed on the water-bath, and the solution was poured into light petroleum in order to precipitate the oxazole completely. The yield was nearly theoretical. The product, when crystallised from alcohol, separated in fine, white needles, which melted at 216° :

0.1781 gave 0.5200 CO_2 and 0.0914 H_2O . $C=79.75$; $H=5.7$.

0.1700 „ 6.55 c.c. N_2 at 16° and 75.35 mm. $N=4.44$.

$C_{21}H_{17}O_2N$ requires $C=80.00$; $H=5.4$; $N=4.45$ per cent.

The tetrahydro-oxazolone is readily soluble in glacial acetic acid or acetone, fairly so in amyl alcohol or toluene, especially on heating, but quite insoluble in light petroleum.

The compound is very stable; attempts to reduce it with sodium amalgam, or even with sodium in amyl alcohol, yielded the unchanged substance, and phosphorus trichloride was found to be without action on it. No salts with hydrochloric acid or picric acid could be prepared.

*α -Hydroxy- β -*m*-toluidino- $\alpha\beta$ -diphenylethane, $C_{21}H_{21}ON$.*

This compound was prepared from *α -keto- β -*m*-toluidino- $\alpha\beta$ -diphenylethane* (McCombie and Parkes, *loc. cit.*, p. 1996) by reduction with sodium amalgam in exactly the same manner as that

described later for the preparation of the β -naphthylamino-compound. It crystallised more easily than that compound from methylated spirit, separating in colourless needles which melt at 133° :

0.1825 gave 0.5544 CO_2 and 0.1180 H_2O . $\text{C}=82.84$; $\text{H}=7.18$.

$\text{C}_{21}\text{H}_{21}\text{ON}$ requires $\text{C}=83.17$; $\text{H}=6.93$ per cent.

4:5-Diphenyl-3-m-tolyl-2:3:4:5-tetrahydro-2-oxazolone.

This compound after recrystallisation from methylated spirit (in which it is only sparingly soluble), or from amyl alcohol, melted at 189° :

0.1808 gave 0.5329 CO_2 and 0.0906 H_2O . $\text{C}=80.38$; $\text{H}=5.57$.

$\text{C}_{24}\text{H}_{19}\text{O}_2\text{N}$ requires $\text{C}=80.24$; $\text{H}=5.78$ per cent.

4:5-Diphenyl-3-p-tolyl-2:3:4:5-tetrahydro-2-oxazolone.

When recrystallised from amyl alcohol or methylated spirit this substance melted at 209° :

0.1846 gave 0.5440 CO_2 and 0.0985 H_2O . $\text{C}=80.37$; $\text{H}=5.93$.

$\text{C}_{24}\text{H}_{19}\text{O}_2\text{N}$ requires $\text{C}=80.24$; $\text{H}=5.78$ per cent.

*α -Hydroxy- β -2-naphthylamino- $\alpha\beta$ -diphenylethane,
 $\text{OH}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$.*

This substance was prepared from the corresponding keto-compound by reduction with sodium amalgam.

To 10 grams of α -keto- β -2-naphthylamino- $\alpha\beta$ -diphenylethane dissolved in 100 c.c. of methylated spirit were added 50 grams of freshly prepared sodium amalgam (4 per cent.), and the mixture was kept almost at the boiling point for two to three hours. It was not found necessary to dissolve the compound completely in alcohol, for as the reduction proceeded, the compound was dissolved. The solution became dark in colour, and when reduction was complete, the solution was poured into boiling water, and allowed to remain for several hours before filtering. The separated solid was washed with dilute hydrochloric acid to remove any naphthylamine, and was then boiled with a small quantity of light petroleum until a white product was obtained. The mixture was cooled, the liquid was decanted from the white solid, and the latter was recrystallised from a larger bulk of light petroleum. Unless the impurities were removed by a preliminary extraction with light petroleum, recrystallisation was found to be impossible.

When pure, this substance is a white, crystalline solid, extremely

soluble in all ordinary solvents, except light petroleum, from a large quantity of which it crystallises well and melts at $124-125^{\circ}$:

0.1831 gave 0.5694 CO_2 and 0.1011 H_2O . $\text{C}=84.81$; $\text{H}=6.14$.

$\text{C}_{24}\text{H}_{21}\text{ON}$ requires $\text{C}=84.95$; $\text{H}=6.20$ per cent.

4:5-Diphenyl-3- β -naphthyl-2:3:4:5-tetrahydro-2-oxazolone.

The recrystallised hydroxy-compound was dissolved in hot benzene, and, from time to time, small quantities of a 20 per cent. solution of carbonyl chloride in toluene were added, whilst the solution was kept hot on a sand-bath. After a time a white solid was precipitated, and when excess of carbonyl chloride had been added, the mixture was allowed to remain for some time. The excess of carbonyl chloride was removed by evaporation, and the solution, when cold, was poured into a large excess of light petroleum, which precipitated the oxazolone completely.

The substance when recrystallised from methylated spirit or amyl alcohol separated in large, white, silky needles, which melted at 231° . If the hydroxy-compound was pure, the yield of the oxazolone was nearly theoretical. The solubilities of the naphthyl derivative were very similar to those of the corresponding aniline compound:

0.1772 gave 0.5335 CO_2 and 0.0864 H_2O . $\text{C}=82.13$; $\text{H}=5.42$.

$\text{C}_{21}\text{H}_{19}\text{O}_2\text{N}$ requires $\text{C}=82.19$; $\text{H}=5.21$ per cent.

CHEMICAL DEPARTMENT,
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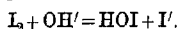
VI. *The Action of Halogens on Silver Salts.*

By HUGH STOTT TAYLOR (1851 Exhibition Scholar,
University of Liverpool).

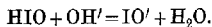
In a recent communication it has been shown by Normand and Cumming (T., 1912, 101, 1852) that the halogens react with silver salts to yield an insoluble silver haloid, an acid, and one or more oxidation products either of the acid or the haloid. In the simpler cases considered, namely, those in which no secondary oxidations occurred, interesting conclusions were drawn as to the variation in the products of reaction with the halogen used; thus (*loc. cit.*, p. 1855), it is pointed out that reactions with iodine usually result in the formation of an iodate. With chlorine and bromine the reactions yield, however, hypochlorous and hypobromous acids.

That iodine is quite analogous to the halogens chlorine and bromine in its action on alkali hydroxides has long been known. Schönbein (*J. pr. Chem.*, 1861, **84**, 385) established this in 1861, and his observations have since been extended and amplified (Berthelot, *Ann. Chim. Phys.*, 1878, [v], **13**, 20; Schwicker, *Zeitsch. physikal. Chem.*, 1895, **16**, 302; Foerster and Gyr, *Zeitsch. Elektrochem.*, 1903, **9**, 1; Skrabal, *Monatsh.*, 1907, **28**, 319; 1911, **32**, 167, 815). It would therefore be expected that in reactions with silver salts a similar analogy would be found to hold.

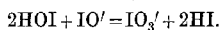
Thus, the interaction of iodine and an alkali yields hypiodous acid according to the equation:



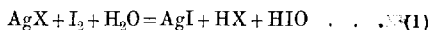
With excess of alkali an equilibrium is set up:



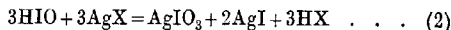
Further, dissolved hypiodites are unstable, and are converted in course of time into iodate according to the equation:



With silver salts, therefore, owing to the insolubility of the silver iodide, the following equilibria would be expected:



With excess of the silver salt the reaction should then proceed to the iodate stage in accordance with the equation:



The mechanism of reaction suggested by Birnbaum (*Annalen*, 1869, **152**, 111) and by Normand and Cumming (*loc. cit.*, pp. 1853, 1854) represents, according to such views, the sum of the two reactions (1) and (2).

As is evident from a study of the action of iodine on alkali hydroxides, the alkali hypiodites are much less stable than the corresponding salts of chlorine and bromine, conversion to iodate occurring with a much greater velocity than is the case in the formation of chlorate or bromate. The velocity of conversion, also, is accelerated by rise of temperature and increase of concentration. It is probable, therefore, that with silver salts also the initial formation of hypiodite will be the more easily demonstrable the lower the temperature of experiment and the smaller the concentration of the solutions employed. The validity of these assumptions was tested with iodine and silver nitrate in the following experiments, which were carried out some months previous to the appearance of the paper by Normand and Cumming. The analogous experiments with silver acetate have been performed subsequent to the publication of the work in question.

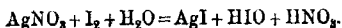
R. L. Taylor (*Mem. Manchester Phil. Soc.*, 1897, [viii], 41, 1) in a paper on hypiodous acid and hypiodites first demonstrated that silver nitrate reacts with aqueous iodine solutions, the resulting solution giving all the reactions for hypiodite. By titrating the solutions obtained with a standard solution of indigo-carmin, the author showed that the bleaching action immediately after the addition of silver nitrate corresponded with the formation of 95 per cent. of the hypiodite demanded by theory. Further, it was shown that the solution so obtained was extremely unstable, and that after five minutes it had lost 90 per cent. of its bleaching power.

EXPERIMENTAL.

Method of Estimation of Hypiodite.

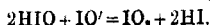
It was noticed by R. L. Taylor that considerable uncertainty attaches to titration with indigo-carmin. With iodine-water an excess of indigo may be added and apparently bleached, but on keeping the blue colour returns. Similar difficulties were observed in the initial stages of the present investigation. Consequently, the method was rejected in favour of Schwicker's method (*Zeitsch. physikal. Chem.*, 1895, 16, 303). By the addition to a hypiodite solution of excess of a solution of sodium hydrogen carbonate saturated with carbon dioxide and also a solution of an iodide, it was shown by Schwicker that iodine is liberated equal in amount to twice the amount of iodine present as hypiodite. The iodine liberated can then be titrated with sodium arsenite solution.

Silver Nitrate and Iodine.—An aqueous solution of iodine when treated with a solution of silver nitrate yields a pale yellow liquid containing silver iodide in a finely divided condition. If the volumes of the solutions are so chosen that equimolecular quantities of the two substances react, the solution obtained, when tested immediately for hypiodite by the method of Schwicker, gives a titre corresponding on an average with the formation of 96 per cent. of the amount of hypiodite required according to the equation:



If the amounts taken are in the ratio of one atom of iodine to one molecule of silver nitrate, immediate titration for hypiodite demonstrates the presence of about 90 per cent. of the total hypiodite required by theory.

The low values obtained are due to the rapid decomposition of the hypiodite into iodide and iodate according to the equation:



The hydriodic acid formed is removed as insoluble silver iodide.

vol. chl.

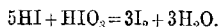
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34 TAYLOR: THE ACTION OF HALOGENS ON SILVER SALTS.

The decomposition is the more rapid the greater the concentration of silver salt present, as is evident from the following time reactions effected with solutions containing approximately 1, 2, and 3 molecules of silver nitrate respectively for each molecule of iodine. The method of procedure adopted in these experiments was to take a given volume of solution containing the materials in the required proportions, and then to titrate aliquot portions thereof at definite intervals of time. The first column indicates the time in minutes intervening between mixing and titration, the remaining columns the percentage of hypiodite present.

Time.	Percentage hypiodite with 1 molecule iodine and		
	1 mol. AgNO ₃ .	2 mols. AgNO ₃ .	3 mols. AgNO ₃ .
1	92.5	72.8	35.5
3	81.8	53.6	—
6	76.2	38.0	10.5
11	71.0	24.0	6.9
16	68.7	—	4.5
21	67.3	14.2	3.3
28	—	10.5	—
80	64.5	—	—

In the first example in which the materials are present in approximately equimolecular quantities, the hypiodous acid is slowly converted into hydriodic acid and iodic acid. In its initial stages the conversion is assisted by the slight excess of silver salt necessary for the attainment of the first reaction, but after a period of time, during which the silver is removed as insoluble silver iodide, the rate of decomposition sensibly diminishes. Further, it is known that a mixture of hydriodic and iodic acids decomposes to yield iodine:



Regeneration of iodine would therefore be expected in the progress of the above reaction. That this occurs can be demonstrated by treating a mixture of molecular quantities of iodine and silver nitrate solutions with starch paste. No coloration is observed on addition, but the characteristic blue colour slowly develops.

In more concentrated solutions than it is possible to obtain by using aqueous solutions of iodine, the reaction between silver nitrate and the halogen still proceeds through the hypiodite stage to the iodate. This can be demonstrated by the following experiment. A *N*/20-iodine solution in *N*/10-potassium iodide was treated with an amount of standard silver nitrate sufficient to remove the potassium iodide as silver iodide and to allow two molecules of the silver salt to react with each molecule of iodine present. Even in such concentrated solutions, in which obviously the decomposition of hypiodite is greatly accelerated, it was

possible to show the presence, immediately after reaction, of 5 to 10 per cent. of the total hypoiodite required by theory. The variation in the amount titrated varied with the rapidity with which the reaction was effected.

Silver Acetate and Iodine.—With silver acetate, iodine reacts in the same manner as with silver nitrate. One molecule of iodine in aqueous solution reacts with a molecule of silver acetate, the resulting solution, tested immediately, containing 97 per cent. of the theoretical amount of hypoiodite. With the materials present in the ratio of one molecule of iodine to two molecules of silver salt, immediate titration showed the presence of 90 per cent. of the theoretical amount.

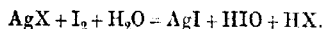
Time reactions with silver acetate present in the ratios of 1:1 and 2 molecules respectively for each molecule of iodine gave the following results:

Time.	Percentage hypoiodite with 1 molecule iodine and	
	1:1 mols. silver acetate.	2 mols. silver acetate.
1	94.7	69.5
3	—	60.7
6	69.3	51.5
11	60.1	38.2
16	52.4	30.9
22	—	27.2
36	50.8	—
50	—	15.6
76	49.3	—

The possibility of following, from the point of view of reaction kinetics, this decomposition of hypoiodite into iodide and iodate is at present the subject of investigation by the author.

Summary.

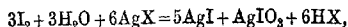
Iodine reacts with silver salts in a manner analogous to that observed in reactions with chlorine and bromine to yield insoluble silver iodide, hypoiodous acid, and another acid. The reaction occurring may be represented by the equation:



Owing to the instability of hypoiodous acid a second reaction occurs, accelerated by rise of temperature, increase in concentration, or presence of soluble silver salts, in which reaction the hypoiodous acid is converted into iodide and iodate. This secondary reaction may be generally represented by the equation:



The simple equation of Birnbaum and of Normand and Cumming,



represents the sum of the two preceding equations.

In conclusion, I wish to express my indebtedness to Prof. Henry Bassett, of University College, Reading, for his valuable assistance and advice during the course of this research.

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UNIVERSITY OF LIVERPOOL

NOBEL INSTITUTE OF PHYSICAL CHEMISTRY,
EXPERIMENTALFÄLTET,
SWEDEN.

VII.—*Diphenylene. Part II.*

By JAMES JOHNSTON DOBBIE, JOHN JACOB FOX, and
ARTHUR JOSIAH HOFFMEISTER GAUGE.

In previous papers dealing with the preparation and properties of 2:2'-dibromodiphenyl it was shown that the action of sodium on this substance results in the formation of the hydrocarbon diphenylene, C_{12}H_8 (T., 1911, 99, 683, 1617). In the experiments by which this substance was first obtained the sodium was employed in the form of thin slices. The reaction proceeded slowly, but gave only a small quantity of by-products. The amount of these was reduced by substituting light petroleum for ether, whereas it was increased by the use of benzene, probably because of the ready solubility of the by-products in this medium. By using finely-divided sodium the rate of the reaction was increased, but the yield of diphenylene was greatly reduced owing to the formation of compounds of high molecular weight. One of these was found by analysis and determination of the molecular weight to have the formula $\text{C}_{64}\text{H}_{56}\text{Br}_2$.

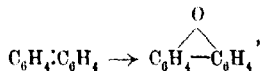
We have made numerous experiments in the hope of finding a more convenient method for the preparation of diphenylene, but so far without success. In one of these attempts *o*-di-iodobenzene was heated with copper powder, both in air and in closed exhausted tubes to 250° . Only resinous products were obtained, from which no diphenylene could be isolated, although there was reason to believe that a small quantity had been formed. Silver diphenate suggested itself as another possible starting point for the preparation of diphenylene. On subjecting this salt to dry distillation it was observed that at a particular temperature sudden decomposition set in, accompanied by much charring and a violent evolution of carbon dioxide. The distillate condensed to a mass of yellow crystals, which dissolved almost completely in light petroleum.

This solution deposited pale yellow crystals, which on recrystallisation melted at 92° . The crystals agreed in character with the lactone described by Graebe and Schestakov (*Annalen*, 1895, **284**, 316) under the name of "biphenylmethylid," $\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}$, and by Griess (*Ber.*, 1888, **21**, 981) and Richter. Bromination of the crystals resulted in the formation of the bromo-derivative melting at 194° prepared by Richter (*J. pr. Chem.*, 1883, [ii], **28**, 294). Their identity with the lactone derived from *o*-hydroxy-diphenylcarboxylic acid is therefore established. The mother liquors from this substance were evaporated to dryness and distilled in a current of steam, when crystals of pure diphenyl were obtained. No trace of diphenylene was found in these operations.

To obtain a supply of material for the further examination of the reactions of diphenylene we were compelled to revert to the original method of preparation described in our first paper on the subject. We have been obliged in consequence to limit our investigation for the present to a few of the simpler derivatives. A dinitrodiphenylene was obtained by heating diphenylene with diluted nitric acid under pressure. By the action of the fuming acid a tetranitro-derivative was formed. Considerable loss of material occurred in both cases, resinous and waxy substances being formed, which were not sufficiently well defined for investigation. Bromine reacted with diphenylene with the formation of two products, namely, 2:2'-dibromodiphenyl and a dibromodiphenylene. By the oxidation of the latter, *p*-bromobenzoic acid was obtained, together with an acid which yielded a strongly fluorescent solution when condensed with resorcinol. The formation of *p*-bromobenzoic acid indicates that under the conditions described substitution takes place in the meta-position with respect to the middle ring.

The behaviour of diphenylene when heated with diluted nitric acid is of special interest. From the products of the reaction three definite substances were isolated, namely, (1) a dinitrodiphenylene, (2) diphenylene oxide, and (3) a nitrophthalic acid. In addition, a quantity of waxy matter of indefinite character was formed.

It is quite clear from the production of diphenylene oxide by the oxidation with dilute nitric acid, on the one hand,



and from the regeneration of 2:2'-dibromodiphenyl on the other, $\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4 \longrightarrow \text{C}_6\text{H}_4\text{Br}\cdot\text{C}_6\text{H}_4\text{Br}$, that the diphenylene molecule is rather unstable. It is probably owing to this instability that

diphenylene forms waxy substances so readily under the influence of various reagents, and that the formation of substitution derivatives is accompanied by so much loss of material.

EXPERIMENTAL.

Finely divided sodium was immersed in dry ether, and dried 2:2'-dibromodiphenyl was added. An immediate reaction resulted, the solution became deep brown, and a quantity of red, insoluble matter separated. The reaction was complete in a very short time. The ether and suspended solid matter were separated from unchanged sodium, and the ethereal liquid was filtered. When the insoluble matter was boiled with a little water to remove sodium bromide a yellow powder was left behind. This dissolved readily in cold benzene and chloroform, from the solution in which it could be precipitated by light petroleum or alcohol. The substance was readily purified by repeated treatment with a mixture of benzene and light petroleum, from which it separated as an amorphous, yellow powder, melting and decomposing at 306°:

0.1246 gave 0.3756 CO_2 and 0.0532 H_2O . $\text{C}=82.2$; $\text{H}=4.7$.

0.1036 „ 0.0312 AgBr . $\text{Br}=12.8$.

0.2876 in 18.74 benzene gave $\text{E}=0.037$. $\text{M.W.}=1180$.

$\text{C}_{84}\text{H}_{56}\text{Br}_2$ requires $\text{C}=82.3$; $\text{H}=4.6$; $\text{Br}=13.1$ per cent.

$\text{M.W.}=1224$.

The formula of this substance may be written $(\text{C}_{12}\text{H}_8)_7\text{Br}_2$ when it is seen to be derived from the action of sodium on two molecules of 2:2'-dibromodiphenyl, the product of which then reacts with a third molecule, and so on until the compound having eighty-four carbon atoms is reached, which is insoluble in ether. The compound $\text{C}_{84}\text{H}_{56}\text{Br}_2$ is similar in character to the compound $\text{C}_{78}\text{H}_{52}\text{Br}_2$ described by Goldschmiedt (*Monatsh.*, 1886, 7, 40) and Hosaeus (*ibid.*, 1893, 14, 323), which results from the action of sodium on the various dibromobenzenes. The ethereal filtrate from the compound $\text{C}_{84}\text{H}_{56}\text{Br}_2$ contains the diphenylene formed in the reaction, together with other substances similar in character to $\text{C}_{84}\text{H}_{56}\text{Br}_2$, but soluble in ether. These may be readily separated from diphenylene by taking advantage of their insolubility in light petroleum or in cold alcohol.*

Bromination of Diphenylene.—The diphenylene to be operated on was covered with water, four times its weight of bromine was added a little at a time, and the whole mass ground up in a mortar. No perceptible rise of temperature resulted, and only a small amount of hydrogen bromide was evolved. The whole mass was

* The behaviour and properties of these substances are not described here, as they have no bearing on the derivatives of diphenylene.

treated with dilute aqueous sodium hydroxide solution until all the unchanged bromine was removed, the residual solid collected, washed with water and a little alcohol, and dissolved in benzene. Colourless needles separated, which did not melt sharply, but after a second crystallisation melted at 80° . This substance was identical with 2:2'-dibromodiphenyl formerly described by us (T., 1911, 99, 1618). The mother liquors on concentration deposited further crops of crystals, of which the first fractions, judging from the low melting point, contained more 2:2'-dibromodiphenyl. The last fractions consisted chiefly of a substance which melted after several crystallisations at 171° , and had the composition of *dibromodiphenylene*:

0.1330 gave 0.1624 AgBr. Br=52.0.

$C_{12}H_6Br_2$ requires Br=51.6 per cent.

The yield of pure substance was not more than 30 per cent., a large proportion of the diphenylene operated on having been converted into 2:2'-dibromodiphenyl and waxy substances of indefinite character containing halogen. Dibromodiphenylene dissolves fairly readily in benzene and alcohol, from which it separates in long, stout, colourless needles. When oxidised by chromic acid it yields a mixture of acids. One of these was recognised as a phthalic acid by the strongly fluorescent solution obtained by condensing it with resorcinol. The other was proved by its equivalent weight and melting point (248°) to be *p*-bromobenzoic acid.

Nitration of Diphenylene.—One part of diphenylene was dissolved in ten parts of concentrated sulphuric acid, and the mixture cooled with ice; four parts of nitric acid (D 1.5) were then added a little at a time, keeping the whole immersed in a freezing mixture. When the action, which at first was very violent, had moderated, the flask containing the mixture was heated on a water-bath for one hour. The contents of the flask after being allowed to cool were poured into ten times their volume of ice-water; the solid which separated was collected, washed with water and a little alcohol, and dried. The yield of crude solid was about 30 per cent. of the weight of the diphenylene taken. The dried precipitate was boiled with a large quantity of alcohol, from which it crystallised on cooling in fine, yellow needles, melting at 223° :

0.2372 gave 0.3768 CO_2 and 0.0304 H_2O . C=43.3; H=1.4.

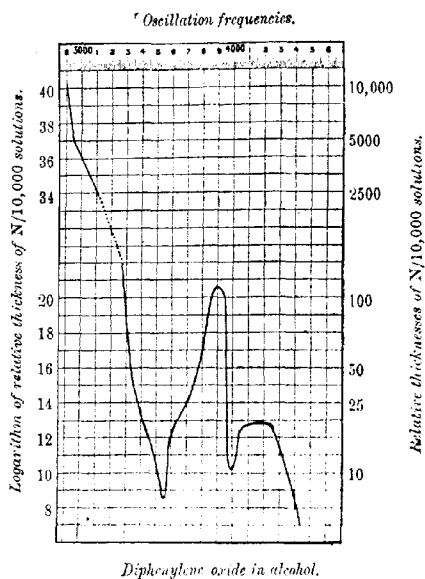
0.1038 „ 15.1 c.c. N_2 at 19.5° and 768 mm. N=17.1.

$C_{12}H_4O_8N_4$ requires C=43.4; H=1.2; N=16.9.

The substance is therefore a *tetranitrodiphenylene*. It dissolves sparingly in alcohol and glacial acetic acid, but is almost insoluble in other organic solvents.

Action of Diluted Nitric Acid on Diphenylene.

Diphenylene was heated in a sealed tube for sixteen hours at 150° with twenty times its weight of diluted acid (D 1.2). Considerable decomposition resulted, and a yellow, semi-crystalline mass remained. This was washed with water, digested with ether, and finally with alcohol and benzene. The residue obtained after this treatment consisted of pale yellow needles, which dissolved sparingly in alcohol. It separated from its alcoholic solution in small needles melting at 204° . Analysis showed that the substance was a *dinitro*-



diphenylene. The yield was small. Dinitrodiphenylene is almost insoluble in ether, benzene, or carbon disulphide, but dissolves sparingly in alcohol, acetone, or glacial acetic acid:

0.1236 gave 0.2678 CO_2 and 0.0334 H_2O . $\text{C} = 59.1$; $\text{H} = 3.0$.

0.1314 „ 13.4 c.c. N_2 at 17° and 761 mm. $\text{N} = 11.8$.

$\text{C}_{12}\text{H}_6\text{O}_4\text{N}_2$ requires $\text{C} = 59.5$; $\text{H} = 2.5$; $\text{N} = 11.6$ per cent.

The ethereal solution was treated with aqueous sodium hydroxide, whereby a small amount of an acid was removed. On evaporating off the ether a waxy mass was left behind, which was redissolved

in alcohol. From the alcoholic solution small plates deposited. On redissolving these plates and treating with picric acid, a picrate separated out from the concentrated alcoholic solution, which on recrystallisation melted at 95°. By acting on the picrate with aqueous sodium hydroxide and extracting the resulting liquid with ether a crystalline solid was obtained melting at 78–79°, and possessing the properties of diphenylene oxide. Its identity with this substance was clearly established by its melting point, the melting point of its picrate, and by its absorption spectrum. The absorption spectrum of diphenylene oxide (see diagram) is strikingly characteristic. It possesses two bands; the head of the larger and more persistent band is at $1/\lambda$ 3530, and of the small narrow band at $1/\lambda$ 4000. The spectrum of the substance from diphenylene is identical with this.

The aqueous liquid remaining after the reaction contained an acid which was purified by means of its sodium salt. It corresponded in molecular weight and in the melting point of its methyl ester with 3-nitrophthalic acid (Ag salt: Found, Ag=49.9. Calc., Ag=50.5 per cent.).

We hope in a future paper to give a more particular account than has yet been possible of the physical properties of diphenylene.

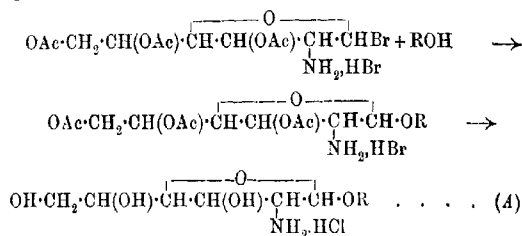
GOVERNMENT LABORATORY,
LONDON.

VIII.—*Synthetic Aminoglucosides Derived from d-Glucosamine.*

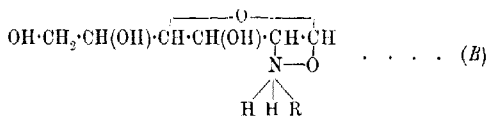
By JAMES COLQUHOUN IRVINE and ALEXANDER HYND, M.A., B.Sc.
(Carnegie Fellow).

THE action of acyl bromides on glucosamine, which was first studied in this laboratory four years ago, has opened up the way for the preparation of glucosamine derivatives of a new type. We have already in previous papers (T., 1911, 99, 250; 1912, 101, 1128) described the use of bromotriacetylglucosamine hydrobromide in the preparation of α -aminomethylglucoside (methylglucosamine), and in the present paper it is shown that the bromo-compound functions as a general synthetic reagent, by means of which the glucosamine residue may be coupled with any hydroxy-compound possessing the requisite solubilities. In this way synthetic aminoglucosides may be prepared, which can be regarded either as derivatives of glucosamine or of glucose.

Expressed in the simplest general terms, the reaction involved consists in the condensation of bromotriacetylglucosamine hydrobromide with a hydroxy-compound in presence of a base which combines with the liberated hydrogen bromide. The product of this first reaction is the salt of a triacetylated aminoglucoside, from which the acyl groups are removed by heating with a dilute solution of hydrogen chloride in methyl alcohol. The most obvious interpretation of the changes is shown in the following scheme:



but in the particular case of α -aminomethylglucoside we indicated that the simple general formula of the type (A) cannot be reasonably applied to the compound, and we suggested the following variation, which includes a modified betaine ring in the molecule:



It appeared to us of interest to prepare a number of aminoglucosides on account of their possible importance as a first step in developing the synthetical chemistry of the glucoproteins, and to ascertain if both types (A) and (B) can exist.

The conclusion arrived at is that, when the group condensed with the glucosamine residue consists of a short open chain, the product possesses properties similar to those of α -aminomethylglucoside, and thus belongs to the type (B). On the other hand, the derivatives of glucosamine which contain a benzene nucleus in the glucosidic position do not differ essentially from true glucosides, except in so far as the properties of the compounds are modified by the presence of the basic amino-group. As examples of this class, to which the general formula (A) applies, we have α -aminobenzylglucoside, α -aminosalicin, α -aminohelicin, and α -aminomorphineglucoside.

So far, then, as generalisations may be made from the data now available, the aminoglucosides related to glucosamine may be

divided into the above two classes, which differ sharply in their properties. Those in which nitrogen is linked to oxygen are remarkably stable towards the hydrolytic action of hydrogen chloride; they are also unaffected by emulsin, and form additive compounds with silver iodide. In sharp contrast to this behaviour, the normal glucosides are easily hydrolysed by acids, and in the case of aminohelicin and aminosalicin are apparently also hydrolysed by emulsin. The general question of the action of enzymes on compounds of both types now described is evidently important, and Prof. H. E. Armstrong has kindly undertaken to extend our experiments in this direction.

Unfortunately, no definite description can be given of the working methods employed to prepare aminoglucosides from bromotriacetylglucosamine hydrobromide, as the process has to be modified to suit each individual case. Reference to the experimental part will show that when the hydroxy-compound to be coupled with the glucosamine residue is a volatile liquid, it should be used in large excess. With liquids of high boiling points, on the other hand, it is necessary to restrict the amount used to one molecular proportion so as to avoid, as far as possible, the inevitable decomposition of the product which results during the removal of the excess of the reagent. With solid hydroxy-compounds, ether, chloroform, or other indifferent solvent may be employed, but in such cases the base used must also be soluble.

The use of bromotriacetylglucosamine hydrobromide is, in fact, beset with difficulties. Owing to the instability of the compound, its limited range of solubility, and the fact that it cannot be employed in solution at temperatures exceeding 60°, its use in synthetical work is much more restricted than that of tetraacetylbromoglucose. Even in successful reactions the yields obtained were in most cases small owing to the difficulty experienced in removing deliquescent by-products. In the following tables lists are given of the aminoglucosides and their constants, the nomenclature employed expressing the relationship of the compounds to *d*-glucose:

TABLE I.

Acetylated Aminoglucosides.

	Decomposition temperature.	$[\alpha]_D^{20}$ in methyl alcohol.	Type.
Triacetyl- α -aminomethylglucoside (HBr) * :	230—233°	+ 20.26°	(B)
Triacetyl- α -aminoethylglucoside (HBr).....	250—251	12.46	(B)
Triacetyl- α -aminoamylglucoside (HBr).....	227°	10.38	(B)
Triacetyl- α -aminobenzylglucoside (HBr) ..	235—236	52.1	(A)
Triacetyl- α -aminohelicin (HBr)	215—216	200° \rightarrow + 43.6	(A)

* T., 1911, 99, 250.

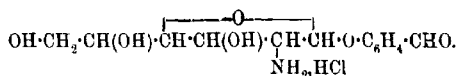
TABLE II.
Aminoglucosides.

	Decomposition temperature.	$[\alpha]_D^{20}$ in water.	Type.
α -Aminomethylglucoside hydrochloride *...	190°	-24.2°	(B)
α -Aminoethylglucoside " ...	213—214	27.75	(B)
α -Aminobenzylglucoside " ...	176	51.15	(A)
α -Aminohelicin " ...	180	8.97	(A)
α -Aminosalicin " ...	178—179	18.99	(A)
α -Aminomorphineglucoside 	246—248	113.45	(A)

* T., 1911, 99, 250.

In addition to the above, a number of cases were examined in which condensation occurred, but the product could not be isolated in the pure state.

Probably the most important compounds now described are the salts of α -amino-*o*-aldehydophenylglucoside and α -aminosaligenin-glucoside, and the constitution of each was accordingly determined so as to establish their relationship with the natural glucosides helicin and salicin. We find that in α -amino-*o*-aldehydophenylglucoside both the amino- and aldehydic groups remain intact; the compound, moreover, has no phenolic or reducing properties. This at once limits the constitution to the formula:



The compound is thus to be regarded as the hydrochloride of α -aminohelicin. At the same time attention should be drawn to the fact that the observations made on the rotatory power of triacetyl- α -aminohelicin seem at first sight in disagreement with this view. The account of this optical behaviour is here given in detail, as an indication of the caution with which changes in rotation must be accepted as a proof of reversible isomeric change.

Pseudo-mutarotation of Triacetyl- α -aminohelicin Hydrobromide.

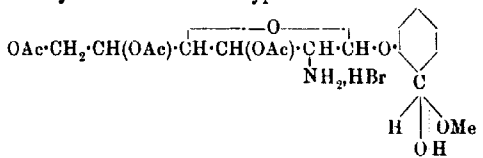
In contrast with the other aminoglucosides examined, the compound now under consideration showed curious optical changes in solution resembling closely those displayed by reducing sugars. When dissolved in methyl alcohol the specific rotation was initially dextro, but rapidly diminished on keeping. An idea of the magnitude and speed of the change can be gained from the following observations:

$$c=1.4943, l=2, t=20^{\circ}.$$

Time from the first reading.	a.	$[\alpha]_D^{20}$.
Minutes 0	+5.98°	+200.09°
" 25	5.88	196.7
" 90	5.04	168.6
" 255	3.93	131.5
Hours 28	2.44	81.63
" 65	1.75	58.54
" 1500	1.30	43.49 (constant)

The curve illustrating the complete optical change was different from the records usually obtained in the case of true mutarotation, in that the initial fall was slow compared with the normal steepness of the curve. Two reactions, one resulting in a slight rise and the other in a pronounced fall in rotatory power, thus appear to proceed simultaneously. The solvent was removed, under the ordinary pressure, from a solution which had attained the permanent rotatory power, and, on the addition of petroleum of low boiling point, the original compound was precipitated in the crystalline state unaltered in melting point and composition. On redissolving this specimen in methyl alcohol the above optical changes were repeated, the solution once more showing downward mutarotation. This behaviour might reasonably be interpreted as indicating that the reducing group of the glucosamine residue had remained unsubstituted, and was thus undergoing the usual $\alpha \rightleftharpoons \beta$ transformation in solution; the precipitation by petroleum in such a case would cause the separation of the less soluble labile form.

We are of the opinion, however, that the rotatory changes referred to are due to temporary combination with the solvent to form a methyl alcoholate of the type:



which readily loses methyl alcohol in the manner indicated by the dotted line. This is supported by the fact that evaporation at $10^{\circ}/12$ mm. of a solution which had attained the permanent rotatory power ($[\alpha]_D + 43^{\circ}$) gave no crystalline product, but a colourless syrup. A portion of this syrup was preserved in a vacuum desiccator for several weeks, when it gradually solidified to a mass of crystals consisting of the original compound. The remainder of the syrup was dried at $40^{\circ}/15$ mm. until constant in weight. A Zeisel estimation then gave $\text{OMe}=5.00$, the theoretical value for

the methyl alcoholate formulated above being $\text{OMe}=5.9$ per cent. Evidently a small amount of the combined methyl alcohol had been expelled during the drying process, and this view was confirmed by the fact that the analysis specimen showed slight mutarotation in the downward sense on being re-dissolved in methyl alcohol. These changes are summarised below, the values being calculated on the concentration of the glucoside salt used:—

Initial $[\alpha]_D$	Permanent $[\alpha]_D$	$[\alpha]_D$ After drying.	Second permanent $[\alpha]_D$
+200.1°	→ +43.5°	→ +73.6°	→ +43.8°
(OMe = Nil).		(OMe = 5.6 per cent.).	

Considerable support was given to this explanation by the fact that aqueous solutions of triacetyl- α -aminohelicin hydrobromide showed a constant rotation when preserved for a week.

Possible Relationship of Aminoglucosides to Glucoproteins.

So far, no simple aminoglucosides of the nature of the compounds described in this paper have been isolated from natural sources, but nevertheless it is highly probable that substances of this type do actually exist in nature. At the present time considerable attention is being directed to the study of the simpler nitrogenous constituents of plants, and the recent work of Schultz and his pupils (*Zeitsch. physiol. Chem.* 1912, **79**, 235, and previous papers) has shown that betaine and complexes containing ring structures similar to betaine are far from being unique, and are widely distributed. Moreover, the proofs given by van Romburgh and Barger of the constitution of hypaphorine, and by Barger and Ewins of the structure of ergothioneine (T., 1911, **99**, 2068, 2336), afford additional examples that betaine complexes of different types must now be regarded as forming a distinct class of natural products.

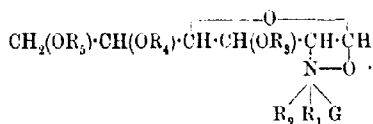
Presumably natural aminoglucosides which possess a betaine-like structure are most likely to occur in organisms in which chitin is deposited as a protective layer, and we have accordingly commenced a systematic search for such compounds in the fungi.

It is also evident that aminoglucosides, derived from glucosamine, possess a special interest, as they may be closely related to glucoproteins. It is true, as Abderhalden has stated, that in the particular case of betaine the compound seems to play no specific part in the protein molecule, and is not likely to be encountered in protein cleavage products. Schultz, who agrees with this view, holds that betaine derivatives resemble alkaloids which, when once formed, take no further part in plant reactions. These statements, however, do not seem applicable to the betaine-like or glucosidic

derivatives of glucosamine where the existence of the potential amino-group and three hydroxyl groups naturally confers considerable reactivity on the molecule.

A review of the somewhat scanty and diffuse information regarding glucoproteins shows that there is at least a strong probability that they are closely related to aminoglucosides, and suggests the possibility of synthesising complexes which would bear the same relationship to glucoproteins that synthetic polypeptides do to proteins; thus the fact that mucins, when boiled with 2.5 per cent. hydrogen chloride, undergo only partial hydrolysis to give non-reducing intermediate products which are only converted into the glucosamine when the hydrolysis is carried out by more concentrated acid, has given rise to considerable discussion. The reaction, however, seems capable of a simple explanation. Hitherto it has been held that this behaviour is a proof that the amino-sugar is not present as such in the protein molecule, but is formed as a decomposition product. Our results on the hydrolysis of acetylated aminoglucosides of the type (B) offer a remarkable parallel to this behaviour, as treatment with 2.5 per cent. hydrochloric acid removes only the substituting acyl groups, and leaves the "glucosidic" residue unaffected. The action of alkalis on the two classes of compound also shows marked similarity. Acetylated aminoglucosides are thus deprived of the acyl groups only, and in the case of glucoproteins the hydrolysis is likewise only partial, and gives non-reducing products. It would thus appear that in the glucoproteins amino-acyl residues occupy the amino-position, and possibly also all the hydroxyl positions with the exception of the glucosidic group. Inspection of the available data on the reactions of glucoproteins seems to us to indicate that at all events some of these compounds may be regarded as analogues of triacetyl- α -aminomethylglucoside, in which the substituting groups are amino-acyl residues, and according to this view the structure would fall into line with Fischer's constitution for tannin (*Ber.*, 1912, 45, 915).

A general formula of this type would be represented by the expression:



where G represents the glucosidic group, and R₁, R₂, etc., stand for amino-acyl residues, which are probably short polypeptide chains. A complex of the above type would give, on hydrolysis with dilute

hydrogen chloride, the amino-acids corresponding with R_1 , R_2 , etc. The latter would also be removed by the action of alkalis, but the residue G would be much more stable to both acids and alkalis.

Consideration of (1) the average carbon, hydrogen, and nitrogen contents of the mucins, (2) the number and amount of the amino-acids formed from them on hydrolysis, and (3) the relative yield of glucosamine salt produced in each case, shows that the above structure is in satisfactory agreement with experimental data.

An alternative structure for the mucins may, however, be considered, namely, that a complex polypeptide chain is simply attached to the glucosamine residue through the amino-group. This structure seems highly unlikely, as not only would the compounds show reducing powers, but hydrolysis in definite stages by means of acids would be less likely to occur, and could in no case give a glucoside. Moreover, it is difficult to imagine, in the case of a long side-chain of this description, that condensation with the free hydroxyl groups would not occur.

The above considerations as to the structure of gluco-proteins are, of course, largely speculative, but are given here in view of the recent appearance of a preliminary note by Hopwood and Weizmann (P., 1912, 28, 261), who describe the action of certain bromoacyl haloids on glucosamine, the obvious extension of their work being the formation of aminoacyl derivatives of the amino-sugar. We think it only right to state here that, during the past two years, workers in this laboratory have also been engaged in introducing bromoacyl residues into glucosamine. Our investigations are, however, directed to the preparation of complexes in which the glucosidic and hydroxyl groups, as well as the amino-group, are substituted, and we take this opportunity of stating that syntheses of the nature indicated in the above theoretical discussion are being vigorously prosecuted.

EXPERIMENTAL.*

Acetylated Aminoglucosides.

Condensation of Bromotriacetylglucosamine Hydrobromide with Ethyl Alcohol.

Triacetyl- α -aminoethylglucoside was, in the first instance, prepared by dissolving bromotriacetylglucosamine hydrobromide (1 mol.) in ethyl alcohol (3 mols.) and pyridine (1 mol.). Although the yield of crude condensation compound thus obtained was quite satisfactory, the removal of the deliquescent by-products proved to be so

* All the reagents employed were pure and were specially dried before use. Except where otherwise stated, evaporations and concentrations were conducted under diminished pressure.

troublesome that the method was abandoned in favour of the following process.

11.7 Grams of the crude bromo-compound, which, as explained in a previous paper (*loc. cit.*), should contain 10 grams of the pure substance, were extracted with excess of cold ethyl alcohol, and the solution filtered from glucosamine salts. Meanwhile, a solution of 6.3 grams of dry morphine in ethyl alcohol had been prepared, and the two solutions were then mixed without delay. The separation of the morphine hydrobromide began in a few minutes, and was complete in twelve hours. Only slightly less than the theoretical amount of the morphine salt was thus obtained. The filtered liquid on concentration yielded two crops of crystalline product, and even the final mother liquor on evaporation to dryness gave a crystalline residue. The total yield was almost quantitative.

After recrystallisation from a concentrated solution in ethyl alcohol, the product was washed with cold alcohol and then with ether. The material used in the following determinations was dried in a vacuum until constant in weight.

Found: C=40.42; H=5.86; Br=19.30; OEt=10.68.

$C_{15}H_{18}O_7N \cdot OEt, HBr$ requires C=40.56; H=5.84; Br=19.30;

OEt=10.87 per cent.

Triacetyl- α -aminoethylglucoside hydrobromide forms colourless needles, which begin to turn brown at 220°, and melt, with complete decomposition, at 250°. The compound gives a very sharp glucosidic reaction with Fehling's solution, and is only hydrolysed into its constituents when boiled with concentrated aqueous hydrogen chloride. Like the other compounds of this type, it is dextrorotatory:

Solvent: Methyl Alcohol. $c=1.806$, $l=2$, $\alpha+0.45^\circ$, $[\alpha]_D^{25}+12.5^\circ$.

Any variation of the method of preparation just described is liable to give complex, uncrystallisable syrups; thus, for example, the use of dry acetone in sufficient amount to dissolve the bromo-compound gave rise to considerable decomposition, the substitution of silver carbonate for morphine gave a similar result, and all attempts to carry out the condensation in absence of a base merely regenerated glucosamine hydrobromide.

Condensation of Bromotriacetylglucosamine Hydrobromide with Amyl Alcohol.

In this particular instance, the condensation is unsuccessful when morphine is used to remove hydrogen bromide. Ten grams of the bromo-compound (1 mol.) were mixed with 5.28 grams of amyl

alcohol (3 mols.) containing 1.50 grams of pyridine (1 mol.). On vigorous shaking, the bulk of the material passed into solution, and, after forty-five minutes, the liquid set to a stiff paste. The reaction was complete in two hours. The solid product, after removal of the excess of amyl alcohol by draining on porous porcelain, was extracted with ethyl alcohol, and the solution, after filtration from glucosamine salts, concentrated in a vacuum desiccator. The product then separated in the crystalline state, and was purified by recrystallisation from ether containing 40 per cent. of ethyl alcohol.

The yields obtained by this process were never more than 20 per cent. of the theoretical amount, and were not improved by any modifications of the method.

Found: C=44.52; H=6.72; Br=17.53.

$C_{12}H_{15}O_7N \cdot C_6H_{11}HBr$ requires C=44.71; H=6.63;

Br=17.52 per cent.

Triacetyl- α -aminoamylglucoside hydrobromide crystallises readily in delicate needles from solutions in ethyl acetate, amyl alcohol, or a mixture of ether and alcohol. The compound, however, shows a marked tendency to separate in a gelatinous form, which only becomes crystalline when stirred with dry ether. The crystals turn brown at 217° , and decompose at 227° . The compound behaves as a glucoside towards Fehling's solution, but is remarkably stable to hydrolysis. Contrary to expectation, all attempts to remove the acetyl groups resulted in profound decomposition, and thus the unsubstituted glucoside was not isolated.

The specific rotation in methyl alcohol for $c=1.687$ was $+10.4^\circ$. It should here be stated that the amyl alcohol used in the preparation of this glucoside showed $\alpha -0.76^\circ$ for $l=1$. The excess of amyl alcohol which remained uncombined was recovered from the tiles and purified. It then showed no appreciable alteration in rotatory power from the original value.

Condensation of Bromotriacetylglucosamine Hydrobromide with Benzyl Alcohol.

The preparation of triacetyl- α -aminobenzylglucoside presented considerable difficulty, and the following process, although far from satisfactory, was the only one to give a crystalline product:

Eighteen grams of the pure recrystallised bromo-compound (1 mol.) were gradually mixed with 4.32 grams of benzyl alcohol (1 mol.), containing 3.18 grams of pyridine (1 mol.). The mobile, syrupy liquid thus obtained gradually gelatinised. The mass was then thoroughly mixed with dry ether, the solvent poured away,

and the residue dissolved in chloroform. On the cautious addition of carbon tetrachloride an oil was precipitated, which was extracted with a mixture of alcohol and benzene. The product crystallised slowly from this solution. Several recrystallisations from a mixture of ether (3 parts) and alcohol (1 part) were necessary to obtain the glucoside salt in a state of purity. The yield was less than 1 gram.

Found: C=47.65; H=5.69; Br=16.63.

$C_{12}H_{18}O_7 \cdot N \cdot O \cdot C_6H_5, HBr$ requires C=47.88; H=5.50;
Br=16.79 per cent.

Triacetyl- α -aminobenzylglucoside hydrobromide melts and decomposes at 235–236°. It does not reduce Fehling's solution, but is readily hydrolysed, and is thus a normal glucoside. The compound is completely decomposed when heated with barium hydroxide solution.

Solvent: Methyl Alcohol. $c=1.372$, $l=2$, $t=20^\circ$, $\alpha+1.43^\circ$,
 $[\alpha]_D^{20}+52.11^\circ$.

Condensation of Bromotriacetylglucosamine Hydrobromide with Salicylaldehyde.

The success of this reaction is entirely dependent on the purity of the materials employed. The purest salicylaldehyde obtainable from Kahlbaum was used, and the bromo-compound was recrystallised until quite colourless. Thirteen grams of triacetyl-bromoglucosamine salt (1 mol.) were suspended in dry ether containing 23 grams of anhydrous pyridine (1 mol.). A solution of 10.8 grams of salicylaldehyde (3 mols.) in dry ether was then quickly added, and the mixture vigorously shaken for an hour, during which time the sides of the bottle became coated with a yellow oil. The clear liquid was poured off, and diluted with petroleum of low boiling point until no further precipitate was formed. In this way the glucoside salt was obtained in excellent yield in golden-yellow needles, which were purified by solution in ether and precipitation with petroleum.

Found: C=46.60; H=4.92; Br=16.40; N=2.91.

$C_{12}H_{18}O_7 \cdot N \cdot O \cdot C_6H_4 \cdot CHO, HBr$ requires C=46.51; H=4.94;
Br=16.32; N=2.86 per cent.

Triacetyl- α -amino-o-aldehydophenylglucoside hydrobromide, when pure, is quite white, but the crystals are usually faintly yellow. The compound begins to turn brown at 170°, and completely decomposes at 216°. The solubility shows great variation with the degree of purity, as minute traces of salicylaldehyde render the compound freely soluble in practically all organic solvents, including ether.

The pure substance is, however, dissolved readily only by the lower alcohols, and sparingly by water. Fehling's solution is reduced only after hydrolysis, the removal of the salicylaldehyde residue taking place with extreme ease.

The constitution assigned to the compound in the introduction is deduced from the following properties. When suspended in nitrous acid solution, nitrogen is evolved, thus indicating the presence of the amino-group. That the compound is a glucoside is shown by its behaviour towards Fehling's solution before and after hydrolysis, and, as a positive result was obtained with Schiff's reagent, the aromatic aldehydic group remains unsubstituted, and is not linked to the sugar residue. No definite hydrazone or oxime could, however, be isolated as the compound was decomposed by phenylhydrazine or hydroxylamine. The addition of ferric chloride to a methyl-alcoholic solution of the glucoside gave only a pale green coloration, which became violet when the solution was diluted with water, but this result was, in all probability, due to slight hydrolysis. The absence of a phenolic group was confirmed by the fact that acidification of the glucoside salt dissolved in sodium hydroxide gave no precipitate. The compound is thus regarded as the salt of triacetyl- α -aminohelicin. The pseudo-mutarotation shown by the compound in methyl-alcoholic solution is described and discussed in the introduction.

Unsuccessful Attempts to Prepare Acetylated Aminoglucosides from Bromotriacetylglucosamine Hydrobromide.

The experiments summarised below refer to reactions in which, as a rule, condensation did occur, but the products could not be isolated in a pure condition in sufficient quantity for detailed examination. In each case the experimental methods employed were varied by the use of different solvents and bases, or by the substitution of sodium derivatives for the free hydroxy-compounds.

Reagent used.	Result.
Ethylene glycol.....	Condensation occurred: product amorphous and deliquescent.
<i>l</i> -Menthol	Condensation occurred, but only a trace of crystalline product was isolated.
Saligenin	Reaction took place, but the acetyl groups were partly removed during the change.
Vanillin }	{ Reaction occurred in each case. The products were however, uncrystallisable syrups.
Quinol }	
Ethyl mercaptan	No reaction.
Phenyl mercaptan	No reaction.

Unsubstituted Aminoglucosides. *α -Aminoethylglucoside Hydrochloride.*

The preparation of this compound from triacetyl- α -aminoethylglucoside was carried out exactly as described (*loc. cit.*) in the case of the corresponding methyl compound. Unless carefully recrystallised material is used in the preparation, the product is liable to be contaminated with the salt of aminomorphineglucoside, which is subsequently described. The hydrochloride of α -aminoethylglucoside is, however, easily obtained pure by crystallisation from ethyl alcohol.

Found: C=39.31; H=7.44; Cl=14.70.

$C_8H_{12}O_4N \cdot OEt_2HCl$ requires C=39.41; H=7.44;
Cl=14.55 per cent.

Solvent: Water. $c=2.6850$, $l=2$, $t=20^\circ$, $\alpha-1.49^\circ$, $[\alpha]_D^{20}-27.75^\circ$.

The compound resembles α -aminomethylglucoside hydrochloride very closely. It crystallises in well-formed, prismatic needles, and is insoluble in organic solvents with the exception of the lower alcohols. It possesses no definite melting point, but turns brown at 195° and decomposes at $213-214^\circ$ (corr.). Towards Fehling's solution the behaviour is characteristic of a glucoside, but hydrolysis only takes place on prolonged boiling with concentrated hydrochloric acid. It may be mentioned that a 1 per cent. solution of the compound in 5 per cent. aqueous hydrogen chloride was unaffected in rotatory power by heating for ten hours at 100° .

 α -Aminobenzylglucoside Hydrochloride.

Owing to the difficulties experienced in obtaining pure triacetyl- α -aminobenzylglucoside hydrobromide it was necessary to modify the usual method of preparing the unsubstituted glucoside. Bromotriacetylglucosamine hydrobromide and dry morphine were mixed in molecular proportions and suspended in dry ether; a large excess (5 mols.) of benzyl alcohol was then added, and the mixture shaken for three days. The dissolved material was then precipitated by the addition of ether, and, after filtration, the solid matter was extracted with cold alcohol. The extract, on evaporation to dryness, gave a semi-crystalline residue, which was shaken with ether and filtered. The product thus obtained was not uniform, and consisted of a mixture of the salts of partly acetylated aminobenzylglucosides, but this did not interfere with the preparation of the unsubstituted glucoside. The complete removal of the acetyl groups was carried out by heating at 70° for three hours with methyl alcohol containing

2 per cent. of hydrogen chloride, and the further treatment did not differ in any essential respect from the other hydrolyses described. The crude product was purified by solution in methyl alcohol and fractional precipitation with ether.

Found: C=50.90; H=6.78; Cl=11.56.

$C_6H_{12}O_4N \cdot O \cdot CH_2 \cdot C_6H_5 \cdot HCl$ requires C=51.03; H=6.59;
Cl=11.60 per cent.

In crystalline form, solubilities, and behaviour towards Fehling's solution the compound resembles the other aminoglucosides described; it is, however, easily hydrolysed. The salt decomposes after preliminary browning, at 176° (corr.), and shows in aqueous solution ($c=1$) the specific rotation -51.2° .

α -Aminohelicin Hydrochloride.

The removal of the acetyl groups from triacetyl- α -aminohelicin was complete on boiling in methyl alcohol containing 2 per cent of hydrogen chloride for ninety minutes. During this process the specific rotation diminished from $+192^\circ$ to $+13.7^\circ$. The product was isolated in the form of the hydrochloride in the usual manner, and was crystallised from ethyl alcohol containing a little ether.

Found: C=48.56; H=5.77; Cl=11.94.

$C_6H_{12}O_4N \cdot O \cdot C_6H_4 \cdot CHO \cdot HCl$ requires C=48.81; H=5.68;
Cl=11.10 per cent.

α -Aminohelicin hydrochloride crystallises in prismatic needles, which decompose at 180° (corr.). The solubilities resemble those of the other aminoglucoside salts, but the compound is unique with respect to the ease with which it is hydrolysed. The specific rotation in water was -8.97° (without mutarotation), but this value is liable to correction, as the specimen appeared to contain a trace of glucosamine hydrochloride.

α -Aminosalicin Hydrochloride.

A solution of dry saligenin (3 mols.) in anhydrous ether was added to finely-powdered bromotriacetylglucosamine hydrobromide (1 mol.), the mixture shaken for several hours, and put aside for one day. The ethereal layer, which was strongly acid, was then decanted, the solid residue washed with ether, and the treatment with saligenin repeated. The mixture was in this case boiled for five hours. After filtration, the solid residue was washed with ether and extracted with cold methyl alcohol. The solution thus obtained on evaporation to dryness gave a syrupy residue consisting of a mixture of the salts of the partly acetylated derivatives of α -aminosalicin. This was hydrolysed in the usual manner in methyl

alcoholic solution. During this change the solution became very dark, but the colour disappeared on neutralisation and subsequent treatment with animal charcoal. The crude salt was crystallised from methyl alcohol, and amounted to 20 per cent. of the weight of the bromo-compound originally used.

Found: C=48.20; H=6.36; Cl=11.11.

$C_6H_{12}O_4N \cdot O \cdot C_6H_4 \cdot CH_2 \cdot OH, HCl$ requires C=48.51; H=6.27;

Cl=11.02 per cent.

α -Aminosalicin hydrochloride crystallises in colourless prisms, which decompose at 179° (corr.). The compound shows the usual glucosidic reaction with Fehling's solution, and is hydrolysed slowly on heating with 5 per cent. aqueous hydrogen chloride. The specific rotation in water ($c=3.606$) was -18.99° , and no mutarotation was detected. No colour reaction was given by ferric chloride solution, and thus the coupling of the glucosamine and saligenin residues must take place through the phenolic group.

α -Aminomorphineglucoside.

In all the condensation reactions involving bromotriacetylglucosamine in which morphine was employed to remove hydrogen bromide, a small proportion of the base reacted with the bromo-compound. This was notably the case in the preparation of the methyl- and ethyl-aminoglucosides, where the morphine was used in solution. The essential product of this side-reaction is an acetylated aminoglucoside of morphine, which is found in the mother liquors after recrystallisation of the crude triacetyl- α -aminoglucoside salts.

The material thus collected in the course of experiments involving the decomposition of 30 grams of the bromo-compound was hydrolysed in the usual manner by boiling for three hours in methyl alcohol containing 2 per cent. of hydrogen chloride. The liquid was then neutralised with silver carbonate, decolorised with charcoal, and concentrated to a syrup. The residue crystallised on keeping, and, after draining on porous porcelain, the crystals were purified by solution in methyl alcohol and fractional precipitation with ether.

Found: C=61.77; H=6.92.

$C_6H_{12}O_4N \cdot O \cdot C_{17}H_{18}O_2N$ requires C=61.84; H=6.78 per cent.

α -Aminomorphineglucoside crystallises in needles, which become brown at 160° and decompose at 248° . The compound has no action on Fehling's solution, but is very easily hydrolysed to give morphine and glucosamine salts. The specific rotation in methyl-alcoholic solution ($c=1$) was -113.5° . The properties of the com-

pound showed that in its formation the reducing group of the sugar residue is coupled to the alkaloid through condensation with a hydroxyl group. This was confirmed by the fact that the base gave a glucosidic *dihydrochloride*. This crystallised in diamond-shaped plates, which decomposed at 204° (corr.).

Found: Cl=13.53.

$C_6H_{12}O_4N \cdot O \cdot C_{17}H_{18}O_2N, 2HCl$ requires Cl=13.65 per cent.

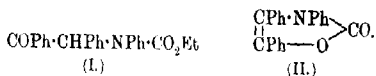
The authors gratefully acknowledge a research grant received from the Carnegie Trust in aid of the above investigation.

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IX.—*The Condensation of α -Keto- β -anilino- α -phenylethane and its Homologues with Carbonyl Chloride, Phenylcarbinide, and Phenylthiocarbimide.*

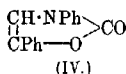
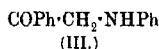
By HAMILTON MCCOMBIE and HAROLD ARCHIBALD SCARBOROUGH.

It has been shown by McCombie and Parkes (T., 1912, 101, 1991) that dihydro-oxazolones can be obtained from α -keto- β -anilino- α -diphenylethane by two methods, namely, (i) the ketone was converted into its carbethoxy-derivative (I), which on treatment with potassium hydroxide in alcoholic solution lost the elements of alcohol with the formation of 3:4:5-triphenyl-2:3-dihydro-2-oxazolone (II); (ii) by the direct action of carbonyl chloride in toluene solution on the keto-compound, in the presence of pyridine, the same dihydro-oxazolone was produced:



Attempts have now been made to extend this reaction to the preparation of dihydro-oxazolones containing one phenyl group less than the compounds described by McCombie and Parkes. The starting point for this work was α -keto- β -anilino- α -phenylethane (III), which is easily prepared from *o*-bromoacetophenone by condensation with aniline. Attempts to prepare dihydro-oxazolones from this compound through the carbethoxy-derivative failed, as all attempts to prepare the latter yielded only the unchanged ketone. Success, however, attended the efforts when the second

method of synthesis was employed. α -Keto- β -anilino- α -phenylethane, in the presence of pyridine, when condensed with carbonyl chloride in toluene solution, yielded 3:5-diphenyl-2:3-dihydro-2-oxazolone (IV) in almost quantitative yields:



By similar condensations the corresponding *o*-, *m*-, and *p*-tolyl and β -naphthyl derivatives were obtained, these substituents being in each case attached to the nitrogen atom. The α -naphthyl derivative could not be prepared, but some of the substance was formed, and floated in the toluene layer, but could not be isolated and recrystallised.

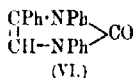
These dihydro-oxazolones are very stable, the presence of the double bond did not lead to the addition of bromine, and the hydrogen atom in position 4 could not be substituted by bromine. The basicity of these compounds is so slight that no hydrochloride or picrate could be isolated.

Compounds similar to the sulphinazoles described by McCombie and Parkes (*loc. cit.*) might have been expected to arise from these ketones by condensation with thionyl chloride instead of carbonyl chloride. With α -keto- β -anilino- α -phenylethane and thionyl chloride, however, no change took place, the compound being recovered unchanged. With the analogous *p*-toluidine and β -naphthyl compounds a black, tarry mass was obtained, from which no crystalline product could be isolated; thus, thionyl chloride appears incapable of forming ring compounds with this series of ketones.

Brazier and McCombie (T., 1912, 101, 2352) have shown that α - β -anilino- $\alpha\beta$ -diphenylethane and its homologues can be condensed into ring compounds of the type 1:3:4:5-tetraphenyl-2:3-thi-2-glyoxalone (V) by condensation with phenylcarbimide. This synthesis has now been extended to include a series of dihydro-

These having one phenyl group less.

α -phenyl phenylcarbimide was condensed with α -keto- β -anilino-2-glyoxalone (III) there resulted 1:3:4-triphenyl-2:3-dihydro-2-oxazolone (VI):

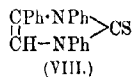
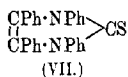


By similar condensations the homologous tolyl and β -naphthyl derivatives were obtained. The α -naphthyl derivative could not be isolated; a tarry mass was formed, which could not be recrystallised.

These glyoxalones are stable compounds, and their basicity is of such an order as to give rise to picrates but no hydrochlorides. *o*-Tolylglyoxalone did not form a picrate which could be isolated, but the evidence seems to show that one is formed in hot glacial acetic acid solution.

Brazier and McCombie (*loc. cit.*) found that two series of picrates were formed by the glyoxalones which they described, the series depending on the group attached to the nitrogen atom in position 3, and that the colour varied with the composition. Only one series of picrates was formed with these new glyoxalones, in which one molecule of the acid was combined with one molecule of the base, and the colours of the picrates varied between deep orange and red.

It has been shown by Brazier and McCombie (*loc. cit.*) that phenylthiocarbimide condenses with α -keto- β -anilino- $\alpha\beta$ -diphenylethane to give 1:3:4:5-tetraphenyl-2:3-dihydro-2-glyoxalthione (VII). This condensation has been extended so as to give a series of dihydroglyoxalthiones containing one phenyl group less; thus, when phenylthiocarbimide reacted with α -keto- β -anilino- α -phenylethane we obtained 1:3:4-triphenyl-2:3-dihydro-2-glyoxalthione (VIII):



By a similar series of condensations, the analogous *o*-, *m*-, and *p*-tolyl compounds were obtained. The α - and β -naphthyl compounds could not be isolated, as all attempts at crystallisation of the α -naphthyl derivative resulted in a viscid, syrupy liquid, and the β -naphthyl derivative gave a white, crystalline substance melting at 166–167°, and having a nitrogen content of 7.30 per cent.

EXPERIMENTAL.

3:5-Diphenyl-2:3-dihydro-2-oxazolone (IV).

This compound was prepared by dissolving 2.1 grams ^{retro-}adding β -anilino- α -phenylethane in 10 grams of pyridine, ^{cent.} 10 grams of a toluene solution of carbonyl chloride (2s, was The mixture was cooled in ice, and, after eighte^{se}. The poured into dilute hydrochloric acid to remove the^d, floccu-oxazolone was precipitated in the toluene layer as^{2y} boiling lent mass, which was separated by filtration, dec^m toluene, with animal charcoal, and recrystallised three ^{retical}: when it melted at 167–168°. The yield was n/

0.1500 gave 0.4180 CO_2 and 0.0627 H_2O . $\text{C}=76.00$; $\text{H}=4.65$.

0.1500 „ 7.9 c.c. N_2 at 15.5° and 725.3 mm. $\text{N}=5.83$.

$\text{C}_{15}\text{H}_{11}\text{O}_2\text{N}$ requires $\text{C}=75.97$; $\text{H}=4.64$; $\text{N}=5.91$ per cent.

3:5-Diphenyl-2:3-dihydro-2-oxazolone crystallises in white, glis-
tening needles, which are soluble in glacial acetic acid or alcohol
in the cold, and moderately so in most organic solvents on warming.

No salt with picric acid could be prepared in glacial acetic acid
solution, or by fusing with the acid alone. Bromination of the
compound in chloroform solution could not be effected. No hydro-
chloride could be isolated in an alcoholic or a glacial acetic acid
solution.

5-Phenyl-3-o-tolyl-2:3-dihydro-2-oxazolone, $\text{C}_{18}\text{H}_{13}\text{O}_2\text{N}$.

This compound was prepared in the same manner, except that
it was allowed to remain for three days before the condensation
was complete. The yield was 60 per cent. of that required by
theory, and the substance melted at $124-125^\circ$:

0.2000 gave 0.5602 CO_2 and 0.0937 H_2O . $\text{C}=76.4$; $\text{H}=5.20$.

0.2000 „ 9.95 c.c. N_2 at 21° and 752 mm. $\text{N}=5.57$.

$\text{C}_{18}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C}=76.4$; $\text{H}=5.18$; $\text{N}=5.58$ per cent.

α -Keto- β -m-toluidino- α -phenylethane, $\text{C}_{15}\text{H}_{15}\text{ON}$.

This substance was prepared by dissolving 10 grams of ω -bromo-
acetophenone in 40 grams of alcohol, and then adding 11 grams
of m -toluidine. After remaining at room temperature for thirty
minutes, the liquid changed to a yellow, almost solid mass. This
solid was separated and recrystallised three times from alcohol,
when it melted at $113-114^\circ$. The compound crystallises in small,
lemon-yellow needles, which are soluble in all common organic
solvents. The yield was theoretical:

0.2000 gave 0.5866 CO_2 and 0.1216 H_2O . $\text{C}=79.99$; $\text{H}=6.70$.

$\text{C}_{15}\text{H}_{15}\text{ON}$ requires $\text{C}=80.0$; $\text{H}=6.66$ per cent.

The analogous aniline and o -toluidine compounds have been
prepared by Bischler (*Ber.*, 1892, **25**, 2860), the α - and β -naphthyl-
amine derivatives by Kunckell (*Ber.*, 1897, **30**, 575), and the
 p -toluidine compound by Lellmann and Donner (*Ber.*, 1890, **23**,
167). They were prepared more easily by the authors in the
manner described for α -keto- β -m-toluidino- α -phenylethane.

5-Phenyl-3-m-tolyl-2:3-dihydro-2-oxazolone, $\text{C}_{18}\text{H}_{13}\text{O}_2\text{N}$.

This oxazolone is soluble to a greater extent in toluene, and an
increased yield is obtained by evaporating, in a brisk draught,

the toluene layer which is formed on pouring the condensation mixture into dilute acid. The crystals are needle-shaped, and unite to form clotted masses, which melt at 84—85°:

The yield was 60 per cent. of the theoretical:

0.2000 gave 0.5594 CO₂ and 0.0950 H₂O. C=76.29; H=5.27.

C₁₆H₁₃O₂N requires C=76.40; H=5.18 per cent.

5-Phenyl-3-p-tolyl-2:3-dihydro-2-oxazolone, C₁₆H₁₃O₂N.

This compound crystallises from toluene in long needles, which unite to form clotted masses, and melts at 173—174°:

0.2000 gave 0.5608 CO₂ and 0.0950 H₂O. C=76.43; H=5.27.

0.2000 „ 10.05 c.c. N₂ at 21.5° and 748 mm. N=5.59.

C₁₆H₁₃O₂N requires C=76.40; H=5.18; N=5.58 per cent.

5-Phenyl-3-β-naphthyl-2:3-dihydro-2-oxazolone, C₁₉H₁₃O₂N.

This compound crystallises from toluene in shining needles melting at 193—194°:

0.2000 gave 0.5870 CO₂ and 0.0822. C=80.04; H=4.57.

0.2000 „ 8.85 c.c. N₂ at 16° and 739.5 mm. N=4.92.

C₁₉H₁₃O₂N requires C=80.00; H=4.53; N=4.88 per cent.

1:3:4-Triphenyl-2:3-dihydro-2-glyoxalone (VI).

This compound is prepared by heating on a water-bath for three hours a mixture of α-keto-β-anilino-α-phenylethane (2.1 grams) and phenylcarbimide (1.5 grams). A clear solution is first formed, which gradually solidifies. On further heating water is eliminated and a white mass obtained. This mass is dissolved in alcohol, and 1 c.c. of concentrated hydrochloric acid is added, and the solution heated under reflux for three hours. On cooling, the glyoxalone separates in clotted, white masses, which after five recrystallisations melted at 164—165°. The substance can be equally well recrystallised from toluene, and is soluble on warming in all common organic solvents. The yield was 2.5 grams:

0.2010 gave 0.5958 CO₂ and 0.0936 H₂O. C=80.84; H=5.17.

0.1518 „ 12.5 c.c. N₂ at 21° and 735 mm. N=9.01.

C₂₁H₁₆ON₂ requires C=80.76; H=5.12; N=8.97 per cent.

The *picrate* was prepared in a boiling acetic acid solution, from which it crystallises in deep crimson needles melting at 130—131°. This salt is readily decomposed by boiling with water, alcohol, or alkali, with regeneration of the glyoxalone:

0.2094 gave 0.4594 CO₂ and 0.0876 H₂O. C=59.84; H=3.58.

C₂₁H₁₆ON₂·C₆H₅O₇N₃ requires C=59.88; H=3.51 per cent.

3:4-Diphenyl-1-o-tolyl-2:3-dihydro-2-glyoxalone, $C_{22}H_{18}ON_2$.

This compound crystallises from alcohol in small, glistening needles, which melt at 159—160°:

0.2099 gave 0.6251 CO_2 and 0.1066 H_2O . $C=81.15$; $H=5.64$.

$C_{22}H_{18}ON_2$ requires $C=80.98$; $H=5.52$ per cent.

No picrate of this glyoxalone could be isolated, either by fusing with picric acid or by boiling with picric acid in acetic acid solution, although the mixture assumed a deep red colour, similar to that exhibited by the other glyoxalones.

3:4-Diphenyl-1-m-tolyl-2:3-dihydro-2-glyoxalone, $C_{22}H_{18}ON_2$.

This substance crystallises from alcohol in fine, white needles, which unite to form clotted masses, and melt at 135—136°:

0.2152 gave 0.6384 CO_2 and 0.1101 H_2O . $C=80.90$; $H=5.68$.

$C_{22}H_{18}ON_2$ requires $C=80.98$; $H=5.52$ per cent.

The picrate crystallises from glacial acetic acid in deep scarlet, glistening needles, which melt at 126—127°:

0.2061 gave 0.4563 CO_2 and 0.0747 H_2O . $C=60.39$; $H=4.02$.

$C_{22}H_{18}ON_2 \cdot C_6H_3O_7N_3$ requires $C=60.53$; $H=4.02$ per cent.

3:4-Diphenyl-1-p-tolyl-2:3-dihydro-2-glyoxalone, $C_{22}H_{18}ON_2$.

This substance crystallises from alcohol in fine, small needles, which melt at 165—166°:

0.2000 gave 0.5924 CO_2 and 0.1018 H_2O . $C=80.78$; $H=5.65$.

0.3000 „ 23.4 c.c. N_2 at 22° and 748.5 mm. $N=8.65$.

$C_{22}H_{18}ON_2$ requires $C=80.98$; $H=5.52$; $N=8.59$ per cent.

The picrate separates from glacial acetic acid in deep red, glistening needles, which melt at 136—137°:

0.2086 gave 0.4638 CO_2 and 0.0729 H_2O . $C=60.61$; $H=3.88$.

$C_{22}H_{18}ON_2 \cdot C_6H_3O_7N_3$ requires $C=60.53$; $H=3.78$ per cent.

Phenyl- β -naphthylbenzoylmethylcarbamide,
 $CH_2Bz \cdot N(C_{10}H_7) \cdot CO \cdot NHPh$.

If a mixture of α -keto- β -2-naphthylamino- α -phenylethane (2.6 grams) and phenylcarbamide (1.5 grams) is heated very gently on a water-bath, a white product is obtained. This is kept for a short time in contact with alcohol, and is then recrystallised from toluene, when it melts at 167—168°:

0.1390 gave 0.4026 CO_2 and 0.0652 H_2O . $C=78.97$; $H=5.21$.

$C_{22}H_{20}O_2N_2$ requires $C=78.93$; $H=5.26$ per cent.

62 MCCOMBIE AND SCARBOROUGH: THE CONDENSATION, ETC.

This compound, on boiling with alcohol, loses water, and is converted into the glyoxalone.

3:4-Diphenyl-1- β -naphthyl-2:3-dihydro-2-glyoxalone, $C_{25}H_{18}ON_2$.

This substance crystallises from alcohol or toluene in glistening needles, which melt at $175-176^\circ$:

0.2000 gave 0.6074 CO_2 and 0.0903 H_2O . $C=82.83$; $H=5.02$.

$C_{25}H_{18}ON_2$ requires $C=82.87$; $H=4.97$ per cent.

The *picrate* crystallises from glacial acetic acid in orange-brown needles, which melt at $167-168^\circ$:

0.2002 gave 0.4620 CO_2 and 0.0664 H_2O . $C=62.96$; $H=3.70$.

$C_{25}H_{18}ON_2 \cdot C_6H_3O_7N_3$ requires $C=62.93$; $H=3.53$ per cent.

1:3:4-Triphenyl-2:3-dihydro-2-glyoxalthione (VIII).

This substance was prepared by heating 2.1 grams of α -keto- β -anilino- α -phenylethane and 1.7 grams of phenylthiocarbimide in an oil-bath at $130-140^\circ$ for three to four hours. The product was then crystallised from toluene, when it separated in small, glistening needles, melting at $170-171^\circ$. The needles are not quite white even after seven recrystallisations, but have a slight yellow tinge. The compound can be recrystallised from alcohol, and is soluble in most organic solvents. The yield is about 30-40 per cent. of the theoretical:

0.2066 gave 0.5810 CO_2 and 0.0893 H_2O . $C=76.70$; $H=4.80$.

0.1525 „ 11.6 c.c. N_2 at 15° and 744.3 mm. $N=8.68$.

0.2817 „ 0.2019 $BaSO_4$. $S=9.84$.

$C_{21}H_{16}N_2S$ requires $C=76.82$; $H=4.87$; $N=8.57$; $S=9.75$ per cent.

3:4-Diphenyl-1-o-tolyl-2:3-dihydro-2-glyoxalthione, $C_{22}H_{18}N_2S$.

This compound crystallises from toluene in small, glistening needles, melting at $165-166^\circ$:

0.1650 gave 0.4680 CO_2 and 0.0786 H_2O . $C=77.33$; $H=5.29$.

$C_{22}H_{18}N_2S$ requires $C=77.20$; $H=5.29$ per cent.

3:4-Diphenyl-1-m-tolyl-2:3-dihydro-2-glyoxalthione, $C_{22}H_{18}N_2S$.

This substance crystallises from toluene in small, white needles, melting at $168-169^\circ$:

0.1738 gave 0.4920 CO_2 and 0.0836 H_2O . $C=77.29$; $H=5.3$.

$C_{22}H_{18}N_2S$ requires $C=77.20$; $H=5.26$ per cent.

3:4-Diphenyl-1-p-tolyl-2:3-dihydro-2-glyoxalthione, $C_{22}H_{18}N_2S$.

When recrystallised from toluene, this substance separates in long, white needles, which unite to form clotted masses melting at $192-193^\circ$:

0.1533 gave 0.4355 CO_2 and 0.0710 H_2O . $C=77.46$; $H=5.15$.

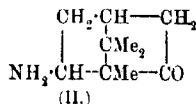
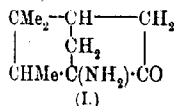
$C_{22}H_{18}N_2S$ requires $C=77.20$; $H=5.26$ per cent.

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X.—Studies in the Camphane Series. Part XXXIII. Orientation of Tiemann's isoAminocamphor.

By MARTIN ONSLOW FORSTER and HUBERT ARTHUR HARRY
HOWARD.

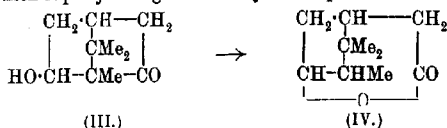
IN addition to ordinary aminocamphor, obtainable by reducing α -nitrocamphor (Schiff, *Ber.*, 1880, **13**, 1404) and isonitrosocamphor (Claisen and Manasse, *Annalen*, 1893, **274**, 90; also Duden and Pritzkow, *Ber.*, 1899, **32**, 1539), and therefore regarded as having the amino-group in the α -position, there exists an isomeric substance discovered by Tiemann (*Ber.*, 1895, **28**, 1082; 1897, **30**, 321), known as isoaminocamphor, which has not been since investigated, and in which the position of the substituent has not been determined. It is true that the discoverer ascribed to it a constitutional formula (I) based on the ideas he then entertained concerning the structure of camphor, but a general survey of the evidence regarded in the light of Bredt's formula for camphor led us to consider the probability of its belonging to the β -series of derivatives, and having accordingly the constitution represented by formula (II):



In the present paper we describe experiments which confirm this view.

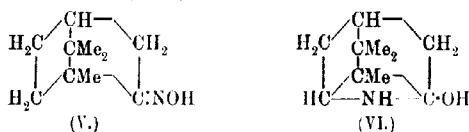
The β -series has hitherto comprised only three mono-substituted derivatives of camphor. The bromo-compound was obtained simultaneously from two sources, namely, the bromide of Reychler's

camphorsulphonic acid (Armstrong and Lowry, P., 1901, 17, 244) and from hydroxycamphene on treatment with bromine (Forster, *ibid.*, 245). β -Chlorocamphor arises from hydroxycamphene and chlorine (T., 1902, 81, 264), whilst the sulphonic acid just mentioned is the third member of the series (Armstrong and Lowry, *ibid.*, 1469). To this group must now be added Tiemann's *iso*-aminocamphor (II) and a new, highly unstable hydroxycamphor (III), which rapidly changes into dihydrocampholenolactone (IV):



Our reasons for making this classification may be summarised in the statement that *iso*-aminocamphor can be produced directly from β -bromocamphor by the action of alcoholic ammonia, whilst indirectly the halogen derivative can be regenerated from the first-named substance. We therefore use the expression β -aminocamphor in place of *iso*-aminocamphor.

The production of β -aminocamphor by Tiemann's process, namely, action of hydriodic acid on camphoroxime (V) must depend on the principle invoked to explain the formation of β -bromocamphor and β -chlorocamphor by the action of halogens on hydroxycamphene (T., 1902, 81, 268). Owing to the strains set up in the camphor molecule it is reasonable to suppose that the β -position approximates in space to the ketonic carbon, thereby facilitating the production of an intermediate compound (VI), which would be a *cyclo*-imino-derivative of hydroxycamphane:

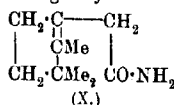
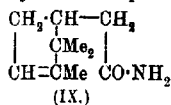


A substance of this structure might be expected to pass readily into the isomeric β -aminocamphor (II), or to be produced easily from it, and we find, in fact, that when the solid hydrochloride of the base in question is heated under diminished pressure, there distils a compound, $\text{C}_{10}\text{H}_{17}\text{ON}$, melting at 71° , and slowly changing at the ordinary temperature into the isomeric β -campholenamide,



melting at 52°. Moreover, when this material (m. p. 71°) is subjected to the treatment which converted hydroxycamphene (VII) into β -bromocamphor (VIII), the latter substance is likewise produced.

Similarly, by the action of chlorine, the compound melting at 71°, and believed to have the constitution (VI), is converted into β -chlorocamphor; moreover, like camphoroxime itself, it is transformed by hydriodic acid into β -aminocamphor, accompanied by a small proportion of campholenonitrile, and we therefore suggest that the conversion of camphoroxime into Tiemann's base depends on the intermediate formation of the *cycloimino*hydroxycamphane (VI). Furthermore, we have found that an attempt to prepare a benzenesulphonyl derivative transforms β -aminocamphor into α -campholenamide (IX), although an aqueous solution of the hydrochloride yields β -campholenamide (X) when gently warmed:



This is the only case in which an α -campholenic derivative has been produced directly from β -aminocamphor, and is therefore comparable with the direct formation of α -campholenic acid by the action of alcoholic alkali on β -bromocamphor (VIII), thus adding support to our contention that the amino-group occupies the β -position.

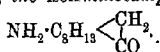
Tiemann found that the amino-group in β -aminocamphor is attached so loosely that treatment with hydroxylamine converts it into two isomeric oximes of α -hydroxycamphor, which he was not able to isolate owing to the readiness with which it passes into dihydrocampholenolactone. We find that semicarbazide also gives two isomeric substances, from which the original amino-group has disappeared, giving place to hydroxyl; the α -semicarbazone melts at 162°, whilst the β -modification melts at 145°, thereupon changing into the less fusible isomeride. Although dilute hydrochloric acid transforms the α -semicarbazone into dihydrocampholenolactone (IV), a distinctly different substance can be produced by hydrolysis with aqueous oxalic acid; this we believe to be the β -hydroxycamphor (III) which Tiemann failed to isolate, because it yields the hydroxycamphoroximes which Tiemann obtained from β -aminocamphor, and changes with hot water into dihydrocampholenolactone (IV).

In connexion with the question of optical activity, it is noteworthy that although camphoroxime and the β -halogen derivatives of camphor are active, β -aminocamphor, as stated by Tiemann,

together with its *p*-toluenesulphonamide and the semicarbazone of β -hydroxycamphor, are optically inactive. A similar case has been recorded by W. H. Perkin (P., 1910, 26, 97) during the synthesis of sylvestrene, when *d*-1-methyl- Δ^1 -cyclohexene-3-carboxylic acid ($[\alpha]_D$ 66°) in the form of its ethyl ester is converted by the Grignard agent into *d*-dihydrocarvestrenol (almost inactive), from which hydrogen chloride produces sylvestrene dihydrochloride ($[\alpha]_D$ 22.6°); the hydrocarbon to which this gives rise is also active, having $[\alpha]_D$ 66.3°.

EXPERIMENTAL.

β -Aminocamphor, the isoAminocamphor of Tiemann,



The preparation of the base described by Tiemann depends on the transformation of camphoroxime by either sulphuric acid (1:1) or hydriodic acid (D 1.96). We find that the latter agent is more convenient if camphoroxime itself is employed, yields of 40 per cent. being usually obtained, but as the remaining product is camphenonitrile, it is more economical to use this material as a source of the base, into which it is converted almost quantitatively by hydriodic acid of the concentration indicated. Since camphenonitrile is readily obtainable from camphoroxime by the action of hydrochloric or sulphuric acid, waste of the more costly hydriodic acid may be reduced to a minimum.

Conversion into α -Camphenenamide.—On attempting to prepare the benzenesulphonyl derivative of β -aminocamphor by agitating an alkaline solution with the calculated amount of benzenesulphonyl chloride, colourless crystals melting at 130° were produced, but the product did not contain sulphur, and was found to consist of α -camphenenamide.

The Toluenesulphonyl Derivative.—Six grams of β -aminocamphor hydriodide dissolved in water and rendered alkaline gave an ethereal solution of the base, which, when dried with potassium carbonate and mixed with 1.9 grams of *p*-toluenesulphonyl chloride, yielded a precipitate of β -aminocamphor hydrochloride during twenty-four hours, whilst the filtrate deposited crystals on evaporation; recrystallisation from benzene diluted with petroleum gave pale yellow needles melting and decomposing at 115°:

0.3480 gave 15.4 c.c. N_2 at 17° and 750 mm. $N = 4.66$.

$\text{C}_{17}\text{H}_{23}\text{O}_3\text{NS}$ requires $N = 4.36$ per cent.

p-Toluenesulphonyl- β -aminocamphor is optically inactive. It is completely hydrolysed by warm alkali to β -aminocamphor and

p-toluenesulphonic acid, but in three hours it is converted by boiling water into dihydrocampholenolactone.

Action of Hydrazine Acetate.— β -Aminocamphor hydriodide, when mixed with hydrazine sulphate and sodium acetate in aqueous solution, deposited during twelve hours a brown, viscous mass, from which dihydrocampholenolactone could be isolated as a result of dissolving in alcohol and diluting with water; the mother liquor, when cooled with ice, gave a crystalline product, which, on recrystallisation from dilute alcohol, reduced ammoniacal silver oxide and mercury acetamide when fresh. In the desiccator, however, this property gradually disappeared, and the melting point rose, with lapse of several weeks, to 178° :

0.1096 gave 17 c.c. N_2 at 26° and 745 mm. $N=17.35$.

$C_{10}H_{18}ON_2$ requires $N=15.38$ per cent.

$C_{10}H_{16}N_2$ „ $N=17.08$ „ „

It would appear, therefore, that the first action of hydrazine is to produce the hydrazone of β -hydroxycamphor, which then undergoes internal condensation, as follows:



Unlike β -aminocamphor, the substance is optically active, a solution containing 0.2680 gram in chloroform, made up to 25 c.c., giving $\alpha_D 40'$ in a 2-dm. tube, whence $[\alpha]_D 31.1^{\circ}$.

Conversion of β -Bromocamphor into β -Aminocamphor.

One gram of the halogen derivative was heated with 20 c.c. of alcoholic ammonia during three hours in a sealed tube at 170° ; 0.5 gram of benzaldehyde was then added to the product, which, after forty-eight hours, was diluted with water. The benzylidene derivative of β -aminocamphor separated, melting at 98° after recrystallisation from dilute alcohol. (Found, $N=5.40$. $C_{17}H_{24}ON$ requires $N=5.49$ per cent.)

In another experiment the liquid, after being heated in the sealed tube, was diluted with water and extracted with ether, this being shaken with dilute hydrochloric acid; on mixing the acid liquid with semicarbazide hydrochloride and sodium acetate, the semicarbazone of β -hydroxycamphor (see below) crystallised in the course of a few hours, melting at 162° . The ethereal liquid left a small quantity of dihydrocampholenimide (m. p. 108°) on evaporation.

Conversion of β -Aminocamphor into β -Bromocamphor.

On heating 5 grams of β -aminocamphor hydrochloride under 30 mm. pressure, a colourless distillate was produced above 180° , solidifying in the receiver; recrystallisation from hot water gave colourless, felted needles, melting at 71° .

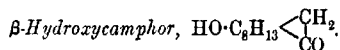
0.1200 gave 8.8 c.c. N_2 at 21° and 755 mm. $N=8.50$.

$C_{10}H_{17}ON$ requires $N=8.44$ per cent.

After several days in the desiccator the substance was found to melt at 52° , having changed into β -campholenamide; this was further identified by hydrolysis to β -campholenic acid, m. p. 51° . Production of β -campholenamide also followed an attempt to prepare a benzoyl derivative in pyridine, whilst α -campholenamide arose when the Schotten-Baumann process was pursued.

As already explained, the initial product of dry distillation (m. p. 71°) is to be regarded as a *cycloimino*-derivative of hydroxycamphane (VI), and might therefore be convertible into β -bromocamphor under conditions which generated that substance from hydroxycamphene. One gram was accordingly dissolved in 10 c.c. of glacial acetic acid, to which 3 grams of anhydrous sodium acetate was added; 1 gram of bromine in 10 c.c. of glacial acetic acid was poured slowly into the cooled liquid, and was decolorised immediately. After fifteen minutes, dilution with water precipitated β -bromocamphor melting at 78° , and having $[\alpha]_D 16.2^\circ$ in chloroform (4 per cent.). It is worth while to emphasise the fact that the product has the same rotatory power as a specimen from hydroxycamphene, because β -aminocamphor is stated by Tiemann to be optically inactive; this property must therefore be due to a fortuitous internal compensation, and not to racemisation of the camphor molecule by hydriodic acid.

On treating the *cycloimino*-compound (m. p. 71°) with chlorine dissolved in glacial acetic acid in presence of sodium acetate, water precipitated β -chlorocamphor, which, after recrystallisation from dilute alcohol, was found to be identical in melting point and specific rotatory power with the substance obtained in the same way from hydroxycamphene.



Three grams of β -aminocamphor hydriodide and 3 grams of sodium acetate having been dissolved in 30 c.c. of water, 1 gram of semicarbazide hydrochloride in 5 c.c. of water was added to the filtered liquid, the crystals separating during twelve hours being

dried in the desiccator before treatment with a small quantity of hot petroleum (b. p. 60–80°), which dissolved the labile β -semicarbazone, leaving the insoluble, stable isomeride. This was recrystallised from benzene diluted with petroleum:

0.0941 gave 15.1 c.c. N_2 at 22° and 750 mm. $N=18.39$.

$C_{11}H_{19}O_2N_3$ requires $N=18.67$ per cent.

The α -semicarbazone of β -hydroxycamphor forms lustrous plates melting at 162°; it dissolves readily in benzene or alcohol, and is optically inactive.

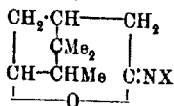
The β -semicarbazone separated as a snow-white, crystalline powder on allowing the filtrate from the initial extraction to evaporate:

0.0996 gave 17.0 c.c. N_2 at 26° and 745 mm. $N=19.09$.

$C_{11}H_{19}O_2N_3$ requires $N=18.67$ per cent.

This modification melted at 145°, above which temperature the fused material solidified; after recrystallisation from benzene diluted with petroleum, it melted at 162°, and did not depress the melting point of the α -semicarbazone.

Hydrolysis of the Semicarbazone.—When the α -semicarbazone was treated with warm, dilute hydrochloric acid, the oily product had the odour of dihydrocamphenolactone, and was ultimately identified as that substance (m. p. 30°). On heating 5 grams of the semicarbazone with 5 grams of oxalic acid in 25 c.c. of water, however, there separated an oil with the odour of borneol; on removing this with ether, and heating an alcoholic solution with hydroxylamine acetate, rapid precipitation of the colourless oxime (m. p. 165°) obtained by Tiemann from β -aminocamphor itself (*Ber.*, 1897, 30, 330) took place. Under similar conditions, dihydrocamphenolactone does not yield an oxime, thus excluding the constitution,



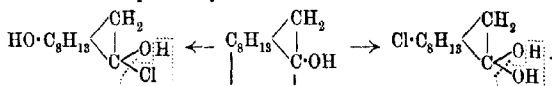
for the oximes and semicarbazones to which β -aminocamphor gives rise.

β -Hydroxycamphor is even more unstable than β -aminocamphor, being more closely comparable with β -dimethylaminocamphor; when heated with water during half-an-hour it is transformed into dihydrocamphenolactone. Tiemann remarks (*Ber.*, 1895, 28, 2170) that on distilling dihydrocamphenolactone prepared by the spontaneous decomposition of aqueous β -aminocamphor hydrochloride at the ordinary temperature, the higher fractions have an odour more camphor-like than that of the lactone itself, and

suggests that at elevated temperatures the lactone is transformed into the hydroxycamphor corresponding with the amino-derivative. He records also an attempt to produce this hydroxycamphor from β -aminocamphor hydrochloride and sodium nitrite, but this led only to dihydrocamphenolactone.

Having produced in the manner described above the substance which we believe to be β -hydroxycamphor, an attempt was made to convert this into β -chlorocamphor by the action of thionyl chloride in presence of dimethylaniline (compare Darzens, *Compt. rend.*, 1911, 152, 1314); this was unsuccessful, however, the sole product consisting of dihydrocamphenolactone. Similarly, application of Darzens' process to the α -semicarbazone of β -hydroxycamphor in the hope of arriving at the semicarbazone of β -chlorocamphor, led to dihydrocamphenolactone. Furthermore, it has to be noted that an attempt to hydrolyse the α -semicarbazone of β -hydroxycamphor with aqueous benzaldehyde failed; benzylidenesemicarbazone was certainly produced, but the other product was dihydrocamphenolactone instead of β -hydroxycamphor.

Since hydroxycamphene gives β -chloro- and β -bromocamphor by the action of chlorine and of bromine, respectively, it seemed possible that hypochlorous acid might give rise to β -hydroxycamphor under similar conditions, although, of course, β -chlorocamphor is the alternative possibility:



The latter, in fact, is the direction taken, a specimen of β -chlorocamphor (m. p. 133°) being obtained. Hydrogen peroxide, which might also have yielded β -hydroxycamphor, left hydroxycamphene unchanged.

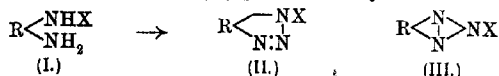
An abridged account of the results of this investigation was presented to the Eighth International Congress of Applied Chemistry, New York, 1912.

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XI.—*The Constitution of the ortho-Diazoimines.*
Part II. The p-Tolyl-β-naphthatriazoles.

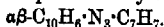
By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT.

THE uncertainty formerly existing in regard to the constitution of the diazoimino-compounds or isotriazoles produced by treating with nitrous acid the aromatic ortho-diamines and their mono-*N*-substituted derivatives (I) has been removed by the results of an investigation by one of us in conjunction with W. Godden, in which it was shown that the two benzenesulphonyl-1:2-naphthylenediamines give rise to isomeric isotriazoles (T., 1910, 97, 1702), thereby demonstrating that the symmetric formula (III) for these diazo-derivatives advocated by Griess must be rejected in favour of the dissymmetric configuration (II) put forward by Kekulé:

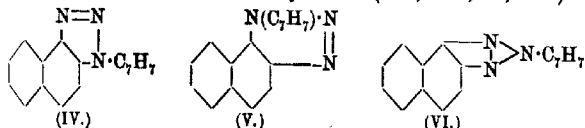


If the constitution indicated by formula (II) is possessed by diazoimino-compounds in general, then when X is an aromatic group it should be possible to obtain three isomerides, two isotriazoles represented by this formula, and one triazole corresponding with formula (III).

In this investigation an attempt has been made to complete the series of three compounds represented by the general formula



One of these was known at the time this research was commenced, namely, 3-*p*-tolyl-1:2-naphthaisotriazole (IV), prepared by Ullmann (*Annalen*, 1904, 332, 103). The triazole (VI) was obtained independently by Charrier and by ourselves from *p*-tolueneazo-β-naphthylamine; the former investigator decomposed this orthoazo-compound by heating to 300°, whereas we employed the chromium trioxide method first introduced by Zincke (*Ber.*, 1885, 18, 3136):

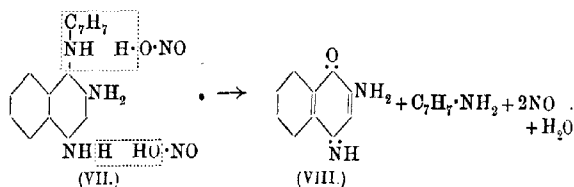


Many attempts have been made to obtain the third isomeride (V) from 1-*p*-tolyl-1:2:4-triaminonaphthalene (VII), a somewhat unstable base obtained by reducing 2:4-dinitro-1-*p*-tolyl-α-naphthylamine, but although various modifications of the diazo-reaction were employed the desired result was not obtained.

With nitrosyl sulphate in 80 per cent. sulphuric acid, followed by treatment with alcohol and copper powder, the triamine underwent condensation, yielding as the main product a complex nitroso-derivative (compare Zincke and Campbell, *Annalen*, 1889, **255**, 351), from which the isotriazole could not be prepared. A small amount of a by-product was isolated, which appeared to be an ethoxy-derivative of the required isotriazole.

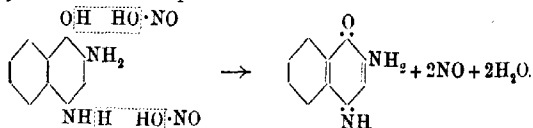
The interaction of nitrous acid or the alkyl nitrites with the triamine and its salts, which takes a totally different course, is very remarkable, inasmuch as neither of the two amino-groups undergoes diazotisation, one being oxidised whilst the other remains unchanged.

The first effect of nitrous acid on the triamine is one of oxidation, the products being 2-amino-1:4-naphthaquinoneimide (VIII) and *p*-toluidine, as indicated by the following equation:



In the presence of hydrochloric acid the quinoneimide is precipitated as its red, sparingly soluble hydrochloride, whereas the *p*-toluidine hydrochloride is diazotised by a further portion of the nitrous acid or alkyl nitrite, so that the filtrate gives an azo-compound with alkaline β -naphthol.

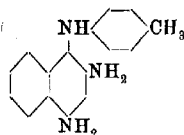
With the object of elucidating the foregoing changes a comparative experiment was made with 2:4-diamino- α -naphthol, when it was found that this substance also undergoes oxidation with nitrous acid or the alkyl nitrites, yielding the same product, 2-amino-1:4-naphthaquinoneimide. This method of preparing the substance is preferable to that in which ferric chloride is employed, and may prove to be of general application in the case of other aromatic polyamines and aminophenols:



The hydrochloride of 2-amino-1:4-naphthaquinoneimide is not diazotisable with sodium nitrite or the alkyl nitrites in aqueous, alcoholic, or glacial acetic acid solutions. Treatment with excess

of nitrosyl sulphate in 80 per cent. sulphuric acid leads to decomposition with loss of a portion of the nitrogen, but there is no indication that any diazotisation occurs.

EXPERIMENTAL.*

1-*p*-Tolyl-1:2:4-triaminonaphthalene,

1-Chloro-2:4-dinitronaphthalene, prepared by following Ullmann's directions (*Ber.*, 1908, **41**, 3932; D.R.-P. 199318), was the starting point in this investigation. Toluene-*p*-sulphonyl chloride (19 grams) recrystallised from light petroleum was added to a solution of 2:4-dinitro- α -naphthol (24 grams) dissolved in redistilled diethylaniline (30 grams), and the mixture heated on the water-bath for two to three hours. After extracting the product successively with *N*-hydrochloric acid, very dilute ammonia, and alcohol (the last solvent being used to remove tarry impurities), the residual 1-chloro-2:4-dinitronaphthalene (yield, 19 grams) melted at 140–141°, and was sufficiently pure for the next operation.

2:4-Dinitro-1-*p*-tolyl- α -naphthylamine,
 $C_{10}H_5(NO_2)_2 \cdot NH \cdot C_7H_7$.

1-Chloro-2:4-dinitronaphthalene (10 grams), dissolved in dry xylene, was boiled for five hours with *p*-toluidine (8.4 grams); *p*-toluidine hydrochloride sublimed into the condenser, and, when diluted with alcohol, the solution yielded a copious, yellow precipitate, which was extracted with warm dilute alcohol to remove *p*-toluidine hydrochloride. The residue, which crystallised well from alcohol, glacial acetic acid, or xylene, separated in felted, yellow needles, and melted at 203–204°, the yield being about 12 grams:

0.1600 gave 18.0 c.c. N_2 at 13° and 745 mm. $N = 13.05$.

$C_{17}H_{13}O_4N_3$ requires $N = 13.00$ per cent.

2:4-Dinitro-1-*p*-tolyl- α -naphthylamine was also obtained by the simultaneous interaction of 2:4-dinitro- α -naphthol, *p*-toluidine, and toluene-*p*-sulphonyl chloride dissolved in dimethyl- or diethylaniline.

The dinitro-compound (1.5 grams) dissolved in 100 c.c. of alcohol

* The earlier experiments in this investigation were carried out by Mr. A. Bramley, B.Sc., A.R.C.Sc., for whose help we desire to express our best thanks.

was reduced by boiling with ammonium chloride (1 gram), zinc (4—5 grams), and a few drops of water. With the large excess of zinc the reduction proceeded fairly readily to a colourless solution with an intermediate dark red stage. The filtrate from the zinc oxy-compounds was diluted with cold water rendered slightly alkaline, the precipitated base was redissolved in *N*-hydrochloric acid, reprecipitated with cold dilute ammonia, stirred until granular, and dried on a porous tile:

0.2208 gave 30 c.c. N_2 at 13° and 766 mm. $N=16.17$.

$C_{17}H_{17}N_3$ requires $N=15.96$ per cent.

1-*p*-Tolyl-1:2:4-triaminonaphthalene is a very oxidisable base, especially in wet solvents. It resinified in air, dissolved in benzene with a certain amount of decomposition, and crystallised in fan-shaped aggregates of glistening, colourless, opaque needles. After two crystallisations the triamine melted at $176-177^\circ$, but further crystallisation led to decomposition.

The triamine, on acetylation, gave rise to a somewhat uncrystallisable product approximating in composition ($N=14.63$ per cent.)

to an ethenyl anhydro-base, $NH_2 \cdot C_{10}H_5 \begin{matrix} \text{N} \cdot C_6H_5 \\ \text{N} : C \cdot CH_3 \end{matrix}$. With *p*-nitrobenzenediazonium chloride the base coupled with difficulty, forming a diazoamino-compound.

Action of Nitrites on Salts of 1-p-Tolyl-1:2:4-triaminonaphthalene.

Alcoholic ethyl nitrite (6 c.c. of a 33 per cent. solution) was added to the triamine (1.6 grams) dissolved in 20 c.c. of alcohol containing 6 c.c. of concentrated hydrochloric acid, when considerable frothing occurred, nitric oxide being evolved; the solution reddened, and a red precipitate slowly separated, whilst the liquid acquired the property of developing an azo-colour with β -naphthol. The red, crystalline precipitate (1.2 grams), which was readily soluble in water, crystallised from the aqueous solution on adding hydrochloric acid in short, dark red needles with a bronzy-green reflex.

The filtrate from these red crystals, when added to alkaline β -naphthol, furnished an azo-compound (1 gram), crystallising from ethyl acetate in garnet-red needles and plates (m. p. $134-135^\circ$), which was identified as *p*-tolueneazo- β -naphthol.

The foregoing red hydrochloride was decomposed with cold dilute ammonia when the orange-yellow, crystalline base was recrystallised from benzene or absolute alcohol; it separated from the former solvent in nodules of orange-yellow needles, decomposing at 167° :

0.1423 gave 19.5 c.c. N_2 at 13° and 760 mm. $N=16.20$.

0.1196 „ 0.3050 CO_2 and 0.0536 H_2O . $C=69.53$; $H=4.98$.

$C_{10}H_8ON_2$ requires $N=16.27$; $C=69.76$; $H=4.65$ per cent.

This base is identical in composition with 2-amino-1:4-naphthaquinoneimide obtained by oxidising 2:4-diamino- α -naphthol with ferric chloride. The dark red hydrochloride when crystallised from dilute hydrochloric acid gave $Cl=17.70$, the calculated amount for $C_{10}H_8ON_2.HCl$ being $Cl=17.02$ per cent.

The foregoing experiment was modified by using ethereal ethyl nitrite, amyl nitrite, and sodium nitrite as sources of nitrous acid, and methyl alcohol and formic acid as solvents. In every case, however, the red hydrochloride was precipitated, even in the presence of copper powder. With sulphuric instead of hydrochloric acid the solution reddened without depositing red crystals, owing to the greater solubility of the sulphate of the amino-quinoneimide. The red precipitate was produced on adding hydrochloric acid.

Action of Nitrous Acid on 2:4-Diamino- α -naphthol.

In order to identify the red hydrochloride produced in the foregoing series of experiments a saturated solution of sodium nitrite (0.9 gram) was added to 1 gram of 2:4-diamino- α -naphthol hydrochloride suspended in concentrated hydrochloric acid cooled by a few lumps of ice. On stirring vigorously the salt of the diamine became replaced by red crystals of 2-amino-1:4-naphthaquinoneimide hydrochloride, the yield being practically quantitative.

When treated with alcoholic or ethereal ethyl nitrite or with sodium nitrite, 2-amino-1:4-naphthaquinoneimide hydrochloride was not diazotised even in the presence of excess of mineral acid. Nitrosyl sulphate in 80 per cent. sulphuric acid decomposed the salt, with the formation of a brownish-yellow compound containing only two-thirds as much nitrogen as the original quinoneimide. In no case could any diazotisation of the 2-amino-group be detected.

The sodium nitrite process for preparing 2-amino-1:4-naphthaquinoneimide hydrochloride from 2:4-diamino- α -naphthol hydrochloride compares favourably with the older method of oxidation with ferric chloride (*Annalen*, 1865, **134**, 377; 1870, 154, 312). A specimen prepared with ferric chloride did not depress the melting point of the product obtained by the foregoing method, but was less easily purified from the oxidising agent.

Action of Nitrosyl Sulphate on 1-p-Tolyl-1:2:4-triamino-naphthalene.

Nitrosyl sulphate (7 grams) was slowly incorporated into an ice-cold solution of the triamine from 3 grams of 2:4-dinitro-1-*p*-

tolyl- α -naphthylamine, dissolved in concentrated sulphuric acid (10 c.c.). Frothing and diazotisation occurred at this stage, and further decomposition of nitrosyl sulphate occurred on adding 4 grams of ice. On adding this solution slowly to 100 c.c. of cold absolute alcohol containing 1 gram of copper bronze, the brown colour changed to yellow, gas was evolved, and a yellow precipitate deposited. After thirty minutes the liquid no longer gave an azo-colour with β -naphthol; the yellow precipitate was then washed with water and crystallised from benzene, when it separated in pale yellow needles decomposing violently at $211-212^\circ$:

0.1298 gave 20.8 c.c. N_2 at 14° and 746 mm. $N=18.46$.

0.1162 „ 0.2952 CO_2 and 0.0428 H_2O . $C=69.26$; $H=4.09$.

0.0990 „ 0.2505 CO_2 „ 0.0372 H_2O . $C=69.06$; $H=4.17$.

$C_{34}H_{24}O_3N_8$ requires $C=68.92$; $H=4.05$; $N=18.92$ per cent.

This formula corresponds with a substance produced by the combination of two molecular proportions of the isotriazole, $C_{17}H_{13}N_3$, with a molecule of nitrogen trioxide, one atom of hydrogen being eliminated from each molecule of triazole. When reduced with zinc and ammonium chloride in dilute alcohol this compound yielded a colourless, oxidisable base, which rapidly became green on exposure to air, and gave yellow salts with the mineral acids, but no diazonium derivative.

The alcoholic filtrate from the foregoing compound and copper powder on dilution with water gave a yellow precipitate readily soluble in benzene, and crystallising therefrom in glistening, orange needles, melting at $234-235^\circ$:

0.1172 gave 13.9 c.c. N_2 at 749 mm. and 11° . $N=13.91$.

$C_{19}H_{17}ON_3$ requires $N=13.86$ per cent.

This formula corresponds with an ethoxynaphthaisotriazole, $C_2H_5O \cdot C_{17}H_{12}N_3$, but the amount of the substance obtained was insufficient for further examination.

2-p-Tolyl-1:2-naphthatriazole.—Chromium trioxide (10 grams) dissolved in 20 c.c. of water was added very slowly to a solution of 10 grams of *p*-tolueneazo- β -naphthylamine (m. p. 113°) in 300 c.c. of glacial acetic acid. After two hours the liquid was poured into cold water, and the insoluble, brown product crystallised from glacial acetic acid, when it separated in light yellow, silky needles, melting at 149° :

0.1573 gave 0.4531 CO_2 and 0.0730 H_2O . $C=78.57$; $H=5.16$.

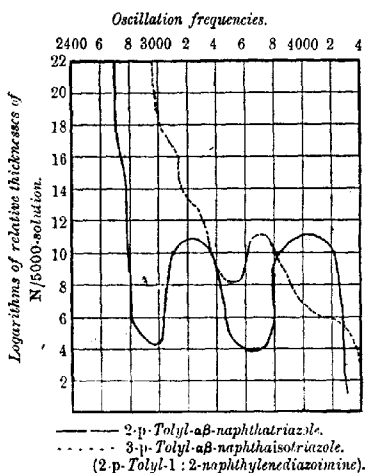
0.2403 „ 33.4 c.c. N_2 at 15° and 748 mm. $N=16.10$.

$C_{17}H_{13}N_3$ requires $C=78.76$; $H=5.02$; $N=16.22$ per cent.

The triazole agrees in properties with the compound obtained by

Carrier on heating *p*-tolueneazo- β -naphthylamine to 300° (*Atti R. Accad. Sci. Torino*, 1910, **45**, 131).

3-*p*-Tolyl-1:2-naphthaisotriazole (Ullmann, *loc. cit.*) was prepared by adding sodium nitrite to a solution of 2-*p*-tolyl-1:2-naphthylenediamine in glacial acetic acid or in alcohol containing hydrochloric acid. When crystallised from alcohol or light petroleum it decomposed at 146–147°. Repeated crystallisation of this substance led to a loss of nitrogen, and the melting point gradually rose to that of 1:2-naphthamethylcarbazole (m. p. 181°). Analysis of the isotriazole decomposing at 146–147° gave C=78.91, H=5.15,



N=16.37, theory for $C_{17}H_{13}N_3$ requiring C=78.76, H=5.05, N=16.22 per cent. The melting point previously recorded for this substance (P., 1910, **26**, 151) was that of a specimen which, as a result of repeated crystallisation, had undergone partial decomposition.

Absorption Spectra.—The two foregoing isomerides were examined spectroscopically in absolute alcohol. The triazole showed two strong bands, with the heads at $1/\lambda$ 2950 and $1/\lambda$ 3650. The isotriazole gives one shallow band at $1/\lambda$ 3500.

We desire to express our thanks to the Research Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation

ROYAL COLLEGE OF SCIENCE FOR IRELAND.
DUBLIN.

XII.—*Co-ordination Compounds of Vanadium. Part I.* *The Acetylacetonates.*

By GILBERT T. MORGAN and HENRY WEBSTER MOSS,
A.I.C., A.R.C.Sc.I.

THE resolution of certain co-ordination compounds of cobalt, chromium, iron, and rhodium into optically active components by Werner and his collaborators has placed on a firm experimental basis the conception of octahedral symmetry as exhibited by these substances, and has facilitated the extension of stereochemical considerations to the chemical constitution of inorganic compounds in general. Two types of co-ordination compounds have been mainly studied from the stereochemical point of view, namely, those in which four and six molecules or radicles are segregated round a central metallic atom.

In the former case the existence of two isomerides having the formula $\text{PtCl}_2 \cdot 2\text{NH}_3$ is taken to indicate that the arrangement of the co-ordination complex around the platinum atom is in one plane, this grouping differing from the tetrahedral arrangement characterising carbon compounds. It is of interest to note, however, that even in the case of carbon compounds the plane configuration has been indicated as a passing phase to explain racemisation (Garner, P., 1912, 28, 67).

In the case of co-ordination compounds containing six radicles or molecules segregated round the central metallic atom as in the case of the hexammine and pentammine (luteo- and purpureo-) chlorides of cobalt and chromium and many other complex salts of these metals, it can scarcely be doubted in the light of present experimental knowledge that the spacial arrangement of these segregating radicles or molecules is that of the octahedron.

Influence of Atomic Volume on Co-ordination.—With the great majority of complex inorganic salts the co-ordination number is either four or six, although in certain instances, for example, potassium molybdenum cyanide, $\text{K}_4[\text{Mo}(\text{CN})_8]$, the co-ordination complex contains eight cyanide groups.

In a recent communication (*Ber.*, 1912, 45, 1322) Ephraïm has considered the influence of atomic volume on the stability of metallic ammine-chlorides having the general formula $\text{R}^{\text{III}}\text{Cl}_2 \cdot 6\text{NH}_3$, and shows that the dissociation pressure of these substances at any fixed temperature, or the dissociation temperature at any fixed pressure, is closely related to the atomic volume of the metal. Those metals with the smallest atomic volume give the most stable hexa-

ammines, and, in fact, no metallic elements with atomic volumes greater than 14 yield compounds of this type which are stable at the ordinary temperature.

On the other hand, metals with high atomic volumes, such as the metals of the alkaline earths (A.V. of Ca=25, Sr=35, Ba=36.5), yield ammine-chlorides of the type $\text{RCl}_2 \cdot 8\text{NH}_3$, whilst zirconium and thorium (A.V. of Zr=21.7, Th=21) give rise to the chlorides $\text{RCl}_4 \cdot 8\text{NH}_3$, from which it would appear that a large atomic volume, whilst decreasing the stability of the complex ammine-salt, leads to an increase in the co-ordination number, irrespective of the value of the principal valency of the metal, since both bivalent and quadrivalent elements give co-ordination compounds of the same order of complexity.

The recognition of co-ordination in inorganic compounds renders necessary a revision of our views on valency. Werner assumes that in addition to principal valencies, which can usually be ascertained by electrolytic means, the central metallic atom possesses a set of auxiliary valencies ("Nebenvalezen") which function in the formation of co-ordination compounds. These auxiliary valencies, like the principal valencies, are apparently to be regarded as integral, so that in its hexammine salts $(\text{Co}_6\text{NH}_3)\text{Cl}_2$, cobalt has a principal valency of 3 and an auxiliary valency of 6, whereas in the pentammine salts, $(\text{Co}_5\text{NH}_3\cdot\text{Cl})\text{Cl}_2$, the metal exerts an auxiliary valency of 5 whilst retaining its principal valency of 3, one of these principal valencies being now implicated in the co-ordination complex.

These hypotheses involve the assumption that chemical affinity is always manifested by valencies which are exact multiples of the adopted unit of valency, namely, that of a univalent atom or group. It seems, however, highly probable that the valencies of elements are not exactly whole numbers, and that even when the integral portions of the valencies have been satisfied there may still remain fractional parts which may, under certain conditions, become operative in the formation of complex substances. This residual affinity may be sufficiently powerful to induce the aggregation which occurs in co-ordination compounds.

If chemical affinity is regarded as an attractive force proceeding equally in all directions from the centre of the sphere occupied by an atom, then the smaller the volume the greater will be the concentration of chemical affinity over its surface and the greater will be the effectiveness of the atom in inducing co-ordination.

Moreover, if chemical affinity is a force which falls off rapidly with the distance from the centre of the atomic sphere, and it may quite conceivably vary inversely as the square, or even as some

higher power of the distance, then a comparatively slight alteration in atomic volume will produce a very marked effect on the stability of the co-ordination compound.

The forces to which these compounds owe their existence cannot be regarded as emanating entirely from the central atom; the residual affinity of this element simply serves as a determining factor. The stability of the arrangement thus initiated is dependent on the mutual attractions exerted on one another by the co-ordinating radicles or groups. It is precisely those radicles or groups which possess considerable residual affinity which function most frequently in the formation of co-ordinated complexes. The general tendency to form hydrated and ammoniated metallic salts is to be attributed in the main to the capacity for association exhibited by water and ammonia molecules respectively. The presence of carbonyl, cyanide, nitrite, and sulphite groups in many stable complexes is similarly to be correlated with the unsaturated nature of these radicles, as contrasted with the saturated carbonate, nitrate, and sulphate groups, which figure less prominently in co-ordination compounds and give rise to less stable aggregations. The halogen radicles appear in many co-ordinated complexes by virtue of their higher valencies.

The size of the atomic volume of the central element has a three-fold influence on the stability of the co-ordination compounds. First, if the atomic volume is small the residual affinity of the atom is exerted in a more concentrated form. Secondly, the co-ordinating molecules or radicles can approach nearer to the centre of the central atom when its volume is small and therefore nearer to one another, so that their mutual attractions become more effective. Thirdly, as the dimensions of the co-ordinating molecules or radicles are of molecular or atomic magnitude, these segregating units will fill more completely the available space round an atom of small volume than that round an atom occupying a larger sphere. This filling up of the available space also conduces to stability, as is manifested by many stereoisomeric compounds.

These speculations are justified by the known facts in regard to co-ordination compounds. The metals forming the most stable complexes are those of the eighth periodic family and their neighbours, and it is precisely these elements among the metals which have the lowest atomic volumes. The three triplets of this group of metals appear each at points of minima on the atomic-volume curve. On the other hand, the alkali metals appearing at points of maxima on this curve give rise to very few co-ordination compounds which are generally extremely unstable.

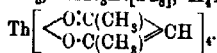
Symmetrical Arrangement of Co-ordination Units about the Central Atom.

If the determining factor in co-ordination is the residual affinity of the central atom which has not necessarily an integral value, and if the formation of the complex is due in part to the mutual attractions of the associating units, then the question arises, what will be the most likely number of units to segregate round the central atom? It is obvious that the most stable system will be that in which there is a symmetrical distribution of the forces interacting between the associating units, and this condition is attained by taking such a number of units that they can be arranged symmetrically over the surface of a sphere. This problem has but few solutions, inasmuch as there are only five regular solids, the tetrahedron, octahedron, cube, icosahedron, and pentagonal dodecahedron, with 4, 6, 8, 12, and 20 vertices respectively. These integers will be the co-ordination numbers corresponding with the theoretically possible most stable systems, and there is ample justification for the belief that molecular aggregations exist corresponding with four of these cases of symmetry, that is, with all the possible cases, except perhaps that of the dodecahedron.

Tetrahedral Symmetry.—The tetrahedron is the form governing the arrangement of units round the carbon atom, and it is noteworthy that this non-metal has the least atomic volume of all the elements. With a larger atomic volume and a segregation of four units there is apparently a tendency for this symmetrical configuration to be replaced by a less regular plane arrangement as in the platino- and pallado-ammines. This plane arrangement has already been referred to as a passing phase for carbon compounds (Garner, *loc. cit.*).

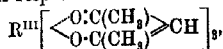
Octahedral Symmetry.—The octahedron is the form corresponding with the vast majority of metallic co-ordination compounds, including most of the very stable complexes of the metals of the eighth periodic family. The isolation of enantiomorphous modifications of such substances as $[\text{Co}_2\text{C}_2\text{H}_4(\text{NH}_2)_2\text{Cl}_2]\text{Cl}$ and $[\text{Co}_2\text{C}_2\text{H}_4(\text{NH}_2)_2\text{Cl}_2]\text{Cl}_2$ is a brilliant confirmation of the existence of this type of symmetry (Werner, *Ber.*, 1911, **44**, 3281; 1912, **45**, 3287).

Cubic Symmetry.—The cube would correspond with the arrangement of groups in such compounds as the following: $\text{K}_4\text{Mo}(\text{CN})_6$, $\text{R}^{\text{II}}\text{Cl}_2\cdot 8\text{NH}_3$, $\text{RCl}_4\cdot 8\text{NH}_3$, $\text{NMe}_3\text{Et}[\text{I}_3]$, $\text{K}_4\text{Th}(\text{C}_2\text{O}_4)_4$, and



Substances having this type of symmetry have been much less extensively studied than those of the octahedral group, and their

investigation will probably show that they present characteristic types of isomerism. Thorium quadriacetylacetonate, for example, should exist in two stereoisomeric non-enantiomorphous modifications, differing in this respect from the teracetylacetonates,



which on account of their octahedral symmetry should be resolvable into optically active enantiomorphous components.

Icosahedral Symmetry.—The icosahedron corresponds with the segregation of twelve associating units round a central atom of which the following complex salts may be examples: the alums, $[R^{III}, 12H_2O]SO_4 \cdot SO_4 R'$; the double chlorides, $[Mg, 12H_2O]PtCl_6$; $[Mn, 12H_2O](AuCl_4)_2$; and the phosphomolybdates, $(NH_4)_3[PO_4, 12MoO_3]$.

Less Symmetrical Aggregations.—The question now arises whether these symmetrical groupings are the only arrangements which obtain throughout the whole range of compounds exhibiting co-ordination.

It might conceivably happen that the atomic volume of an element would be such that the circumjacent space could accommodate a number of associating units not corresponding with any one of the co-ordination numbers derived from the foregoing four regular solids. The arrangement, although not completely symmetrical, might in certain circumstances be capable of existence. Thorium, with an atomic volume of 21, forms the double carbonates $[Th(CO_3)_6](NH_4)_6$ and $[Th(CO_3)_5]Ti^I_6$. The carbonate group generally functions as two associating units, and accordingly these salts may correspond with the arrangement of ten points on a sphere, and with this number of associating units a certain degree of symmetry can be attained.*

* Dr. J. P. Johnston has kindly prepared a model illustrating one of two ways in which a polar symmetry can be developed with this number of points. Two points are taken at the ends of a diameter of a sphere, and round each of these points a small circle is described at an angular distance of $59^\circ 15'$. Squares are inscribed in these circles so that the directions of the diagonals of one are parallel to the bisectors of the angles between the diagonals of the other. The angular distances between consecutive vertices of one square are then equal to the angular distances of its vertices from the adjacent vertices of the other. These angular distances are $74^\circ 51'$ approximately. The solid formed by joining the ten points has sixteen triangular faces, each face being an isosceles triangle.

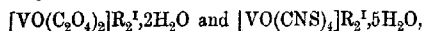
A second arrangement is obtained by describing the circles so that each vertex of the inscribed square is at an angular distance of $65^\circ 30'$ from the adjacent polar point and from each of the adjacent vertices of the other square. The relative orientation of the two squares is the same as in the previous arrangement. The angular distance between consecutive vertices of the same square will then be $79^\circ 32'$ approximately.

Among the elements of the fifth periodic family there are instances of complexes in which it is not easy to bring the co-ordination number into line with the symmetrical groupings based on the octahedron or cube.

In the double fluorides and oxyfluorides it is generally assumed that fluorine and oxygen each function as a single associating unit, as, for example, in Marignac's well known isomorphous series: $K_2TiF_6 \cdot H_2O$, $K_2CbOF_5 \cdot H_2O$, and $K_2WO_2F_4 \cdot H_2O$. It seems reasonable to suppose that these compounds all possess the octahedral symmetry, the co-ordinated complexes being composed in each case of six associating units, F_6 , OF_5 , and O_2F_4 , with oxygen as the spacial equivalent of fluorine in the oxyfluorides.

Although in the foregoing example columbium falls into line with titanium and tungsten in giving the six-membered complex, yet the assumption that oxygen is the spacial equivalent of fluorine does not lead in general to octahedral symmetry in the case of the allied metal, vanadium.

The vanadyl double oxalates and thiocyanates,

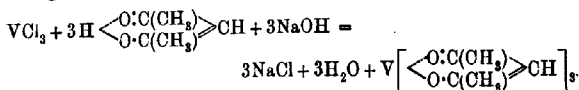


contain five associating units in their complexes, and a similar arrangement obtains in the following isomorphous double fluorides and oxyfluorides: $VF_3 \cdot R^II F_2 \cdot 7H_2O$, $VOF_2 \cdot R^II F_2 \cdot 7H_2O$, and $VO_2F \cdot RF_2 \cdot 7H_2O$.

Here the co-ordination groups would appear to be $5F$, OF_4 , and O_2F_3 respectively. Werner has recognised this difficulty, and endeavours to meet it by bringing a molecular proportion of water into the co-ordination complex, formulating the oxyfluorides $VOF_2 \cdot RF_2 \cdot 7H_2O$ as $[R \cdot 6H_2O][VOF_4 \cdot H_2O]$, in which there are six associating units round the vanadium atom. This formulation could be applied to all the foregoing double salts, since they all contain water of crystallisation, but it is not available in the case of the vanadyl acylacetates described in the present communication, as these compounds crystallise without water from many anhydrous organic solvents.

Anhydrous vanadium trichloride (1 mol.) and acetylacetone (3 mols.) interact in absolute alcohol in the presence of sodium hydroxide or ethoxide (3 mols.), giving rise to vanadium teracetylacetone. As it has not been found possible to combine vanadium directly with carbon through the agency of the Grignard reaction, it is, in the highest degree, probable that in this condensation acetylacetone reacts in its enolic form, so that the metallic atom becomes attached to enolic oxygens by three of its principal valencies, each unsaturated acetylacetone group functioning as two

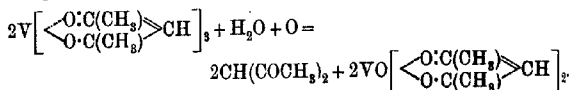
associating units, so that a six-membered complex is developed having octahedral symmetry:



Similar condensations occur with benzoylacetone and acetyl-methylacetone, and the products are in all probability racemic compounds containing two enantiomorphous components:



By oxidation with moist air the vanadium teracetylacetonates give rise to the vanadyl bisacetylacetonates, substances which can also be produced by the direct condensation of vanadyl dichloride and the corresponding acetylacetonate:



These vanadyl bisacetylacetonates are soluble in the ordinary organic media, except ether. Their molecular complexity corresponds with the simplest empirical formula, since a molecular-weight determination in chloroform showed that vanadyl bisacetylacetonate is not associated. The ultraviolet absorption spectra of these compounds agree very closely with those of the teracetylacetonates, and also with those of the acetylacetonates, a relationship which seems to indicate that the acetylacetonate group is in a similar condition in all these substances.

The question now arises, What is the arrangement of the five associating units about the central vanadium atom? Do they form a five-membered complex, or does the group VO function as a single co-ordinating centre attracting to itself four associating units which may be arranged in one plane, as in the case of the platinum-ammines? In either alternative there appears to be a departure from the normal symmetrical arrangement based on the octahedron.

The atomic volume of vanadium (9.3) is considerably greater than that of chromium (7.7), and its co-ordination compounds confirm the foregoing assumption as to the relationship between atomic volume and co-ordination in being less stable than the complexes containing chromium. In aqueous solution the double thiocyanates,

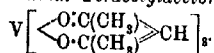
$R_3V(CNS)_3$, are almost entirely dissociated (Cioci, *Zeitsch. anorg. Chem.*, 1899, **19**, 308). Vanadium in the form of the trichloride combines, however, with pyridine and other organic bases, and the products are being examined with the object of obtaining further evidence as to the co-ordination values which obtain in the case of this element.

EXPERIMENTAL.

The anhydrous vanadium chloride employed in the following operations was prepared by heating vanadic anhydride in a stream of carbon disulphide vapour until the residue consisted entirely of vanadium trisulphide. This substance was then heated in a current of chlorine, when sulphur chloride and vanadium tetrachloride distilled over, and were separated by fractionation. During these distillations a portion of the tetrachloride dissociated into vanadium trichloride and chlorine, the unchanged tetrachloride was heated in a reflux apparatus until the brown liquid disappeared, and a dry residue of vanadium trichloride was obtained as a dark purple mass entirely soluble in absolute alcohol, although insoluble in dry Grignard ether (Kay, T., 1880, **37**, 728; Halberstadt, *Ber.*, 1882, **15**, 1619). It has been stated that anhydrous vanadium trichloride is soluble in ether to a green solution. We find, however, that in the absence of water or alcohol the dry chloride is insoluble in this medium.

The more volatile fractions obtained in the foregoing distillations contained in addition to sulphur chloride small quantities of a very volatile vanadium derivative, which was not further examined.

Vanadium Teracetylacetonate,



This compound was prepared most conveniently by adding aqueous sodium carbonate (1.5 mols.) to a mixture of acetylacetone (3 mols.), vanadium trichloride (1 mol.), and chloroform. The co-ordination product, which dissolved in the organic solvent, was isolated by rapid concentration of the solution to a small bulk at the ordinary temperature. The transparent, dark brown prisms or square plates thus obtained were washed with cold alcohol, in which they are somewhat soluble, and were dried on the water-bath in an atmosphere of carbon dioxide:

0.1500 gave 0.2832 CO_2 and 0.0926 H_2O . $\text{C} = 51.5$; $\text{H} = 6.86$.

0.1000 „ 0.0262 V_2O_5 . $\text{V} = 14.67$.

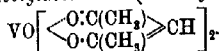
$\text{C}_{15}\text{H}_{21}\text{O}_6\text{V}$ requires $\text{C} = 51.7$; $\text{H} = 6.0$; $\text{V} = 14.7$ per cent.

The teracetylacetonate was also prepared by adding the calcu-

lated amount of alcoholic sodium hydroxide (3 mols.) to a solution of vanadium trichloride (1 mol.) and acetylacetone (3 mols.) in absolute alcohol. The filtrate from sodium chloride was concentrated in carbon dioxide, and the transparent, dark brown prisms which separated were recrystallised from dry ether. The substance is insoluble in water, and dissolves freely in chloroform or benzene; it crystallises from warm acetylacetone in large, well-defined, dark brown plates and prisms. Vanadium teracetylacetonate melts indefinitely at 185—190°,* and can be distilled in small quantities without decomposition.

In the moist condition the teracetylacetonate readily takes up oxygen, and loses a molecular proportion of acetylacetone. During this oxidation the square plates or prisms retain their shape, so that green pseudomorphs after the original compound are produced, consisting of the following vanadyl derivative.

Vanadium Oxybisacetylacetonate (Vanadyl Bisacetylacetonate),



The aerial oxidation of vanadium teracetylacetonate leads to the production of vanadium oxybisacetylacetonate, and this substance can also be prepared by the following method, which is applicable to vanadyl derivatives of other β -diketones.

Vanadic anhydride is reduced to vanadyl chloride by boiling with concentrated hydrochloric acid and alcohol. The blue solution thus obtained is exactly neutralised with aqueous sodium carbonate, the precipitated grey vanadyl hydroxide is washed successively with water and alcohol, and while still moist is dissolved in a warm alcoholic solution of acetylacetone. The green solution on cooling deposits small, bluish-green crystals of vanadium oxybisacetylacetonate, which are washed with alcohol until free from the brown mother liquor. The compound separates from benzene, chloroform, or hot alcohol in hard, transparent, flattened, bluish-green prisms, which are insoluble in water, sparingly soluble in alcohol, and dissolving very readily in chloroform. Although practically insoluble in dry ether, this and the following vanadyl compounds undergo a slight decomposition on digestion with this solvent, a small amount of resinous matter passing into solution:

0.1500 gave 0.2476 CO_2 and 0.0790 H_2O . C=45.02; H=5.86.

0.1500 „ 0.2488 CO_2 „ 0.0758 H_2O . C=45.24; H=5.66.

* The melting point (265—266°) given in the preliminary note (P., 1912, 28, 199) was rendered too high by the presence of the oxidation product, vanadyl bisacetylacetonate.

0.1130 gave 0.0380 V_2O_5 . $V = 18.65$.

$C_{10}H_{14}O_5V$ requires $C = 45.3$; $H = 5.3$; $V = 19.2$ per cent.

Molecular-weight determinations in chloroform by the ebullioscopic method showed that the compound has the simple formula:

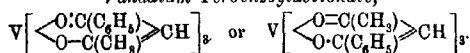
0.1962 in 17.41 $CHCl_3$ gave $\Delta t = 0.161^\circ$. $M.W. = 256$.

0.1688 „ 17.41 $CHCl_3$ „ $\Delta t = 0.139^\circ$. $M.W. = 255$.

$VO(C_8H_7O_2)_2$ requires $M.W. = 265$.

The bisacetylacetonate has no definite melting point, but decomposes and chars at high temperatures.

Vanadium Terbenzoylacetonate,



When alcoholic solutions of vanadium trichloride (1 mol.) and benzoylaceton (3 mols.) are mixed, the green colour of the former substance disappears, and the liquid acquires a clear, brown tint. The addition of alcoholic sodium ethoxide (3 mols.) determines the precipitation of the brown co-ordination compound mixed with sodium chloride. The organic substance was extracted from this precipitate with chloroform, the filtered solution evaporated to dryness, and the resinous residue dissolved in benzene, from which the terbenzoylacetonate separated in dark, chocolate-brown leaflets, melting at $218-220^\circ$:

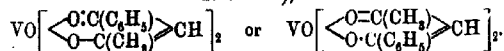
0.1500 gave 0.3632 CO_2 and 0.0784 H_2O . $C = 66.36$; $H = 5.80$.

0.2000 „ 0.0338 V_2O_5 . $V = 9.46$.

$C_{30}H_{27}O_6V$ requires $C = 67.4$; $H = 5.1$; $V = 9.58$ per cent.

The terbenzoylacetonate is insoluble in water, sparingly soluble in alcohol or ether, and dissolves very freely in benzene or chloroform. It is somewhat less oxidisable than the teracetylacetonate, but is slowly decomposed on exposure to moist air, so that after three months a specimen had become largely converted into the bright green vanadium oxybisbenzoylacetonate mixed with long, colourless needles of benzoylaceton.

Vanadium Oxybisbenzoylacetonate (Vanadyl Bisbenzoylacetonate),



Although formed by the aerial oxidation of the preceding compound, this substance is best obtained by the direct interaction of vanadyl hydroxide and benzoylaceton. When the freshly precipitated hydroxide, after washing with water and alcohol, is warmed with an alcoholic solution of benzoylaceton in slight excess, the

hydroxide dissolves, and the resulting green solution deposits immediately emerald-green leaflets of vanadium oxybisbenzoylacetonate:

0.1500 gave 0.3362 CO_2 and 0.0788 H_2O . $\text{C}=61.12$; $\text{H}=5.82$.

0.1500 „ 0.3296 CO_2 „ 0.0627 H_2O . $\text{C}=59.92$; $\text{H}=4.65$.

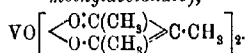
0.2446 „ 0.0590 V_2O_5 . $\text{V}=13.5$.

0.1334 „ 0.0324 V_2O_5 . $\text{V}=13.7$.

$\text{C}_{20}\text{H}_{18}\text{O}_8\text{V}$ requires $\text{C}=61.69$; $\text{H}=4.62$; $\text{V}=13.11$ per cent.

The compound is insoluble in water or ether, sparingly soluble in alcohol, more so in benzene, and very soluble in chloroform. It crystallises from a mixture of chloroform and alcohol in bright green leaflets melting at $214-215^\circ$.

Vanadium Oxybisacetylacetylacetonate (Vanadyl Bisacetylacetylacetonate),



This substance was prepared by the method employed for the other two vanadyl derivatives, freshly precipitated vanadyl hydroxide being dissolved in an alcoholic solution of acetylacetylaceton. It is very soluble in chloroform, sparingly so in alcohol, and insoluble in water or ether. From benzene it crystallises in sage-green, acicular prisms, which decompose and char on heating:

0.1490 gave 0.2740 CO_2 and 0.0860 H_2O . $\text{C}=50.33$; $\text{H}=6.5$

0.1733 „ 0.0535 V_2O_5 . $\text{V}=17.2$.

$\text{C}_{12}\text{H}_{18}\text{O}_8\text{V}$ requires $\text{C}=49.3$; $\text{H}=6.2$; $\text{V}=17.4$ per cent.

Vanadium teracetylacetylacetonate was produced in alcoholic solution by the interaction of vanadium trichloride, acetylacetylaceton, and sodium ethoxide; it is a brown, easily decomposable substance, readily taking up oxygen and passing into the preceding vanadyl compound.

Comparative Study of the Absorption Spectra of Vanadium Trichloride, the β -Diketones, and their Co-ordination Products.

The compounds were dissolved in absolute alcohol to $N/1000$ solutions, and examined in thicknesses of 2, 4, 5, 10, 15, 30, 40, and 50 mm.; the dilution was continued to $N/5000$ solutions, and photographs were taken again at the foregoing thicknesses. The instrument was a one-prism Hilger spectrometer, and the iron arc was used as the source of light.

The ultraviolet absorption spectra of the foregoing acetylacetonates were photographed, and compared with those of their generators, vanadium trichloride, vanadyl dichloride, acetylaceton, acetyl-

methylacetone, and benzoylacetone. Absorption curves were plotted, and those for the acylacetones themselves were found to agree with the results obtained for these substances by Baly and Desch (T., 1904, 85, 1029; 1905, 87, 766).

FIG. 1.

Oscillation frequencies.

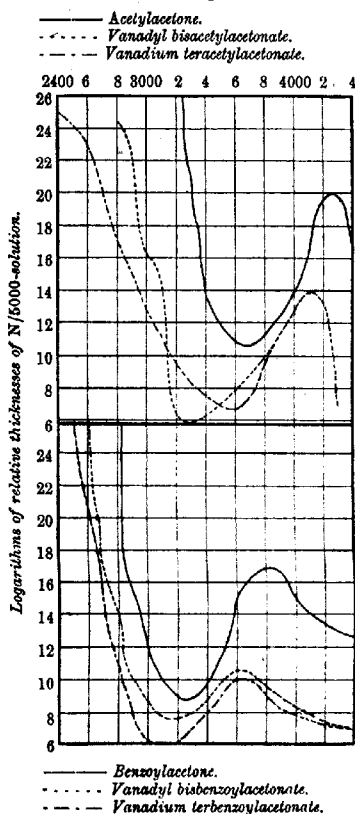
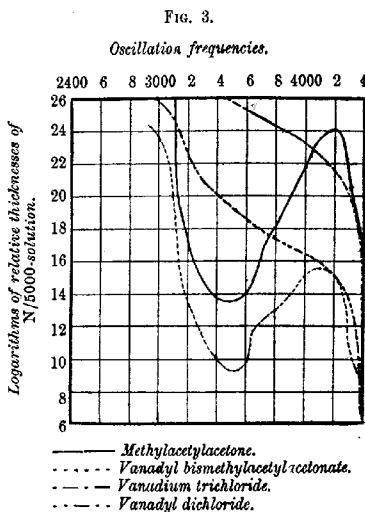


FIG. 2.

The curves for vanadium teracetylacetonate and vanadyl bisacetylacetonate are closely related, and correspond in general form with the curve for acetylacetone, except that they are shifted

towards the red end and the absorption bands are persistent at greater dilutions (Fig. 1). The curves for vanadium terbenzoylacetate and vanadyl bisbenzoylacetate are almost superposable, that of the former compound being slightly more towards the red, with a somewhat more persistent band (Fig. 2). A similar relationship holds between the bands of acetylacetylacetone and vanadyl bisacetylacetylacetone (Fig. 3).

On the other hand, it will be noticed that at these dilutions the



inorganic generators of these co-ordination compounds, vanadium trichloride and vanadyl dichloride, show no absorption bands, but merely general absorption, the curve of the former compound being much further into the ultraviolet than that of the vanadyl compound.

The authors desire to express their thanks to the Research Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

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DUBLIN.

XIII.—*Chemical Reactivity and Absorption. Part II.* *The Variation of Absorption with Concentration.*

By EDWARD CHARLES CYRIL BALY and FRANCIS OWEN RICE.

IN two recent papers (Baly and Krulla, T., 1912, 101, 1469; Baly and Rice, *ibid.*, p. 1475) an explanation of the phenomena of ultra-violet absorption was put forward. It was pointed out that if the affinities of the various atoms in any molecule be considered, it will be evident that a single free molecule must be the centre of a field of force due to the condensation together of the force-lines having their origin in the affinities of the atoms. Clearly the chemical reactivity of any molecule must depend on the free existence of the atomic affinities, and therefore the formation of these condensed force-fields will cause a great decrease in the affinity and the reactivity. If the balance of affinities of opposite type, basic and acidic, within any molecule be complete, then the condensation of the force-lines due to them will also tend to be complete. Such molecules will possess a vanishingly small reactivity.

This condition occurs in the case of simple molecules such as HCl and NH_3 , CO_2 and CaO , and in this is to be found the explanation of the fact that such pairs of substances do not react together in the pure dry state. If the condensed systems be unlocked by some means, then the affinities will become free, and chemical reactivity will begin to make its appearance. One of the possible means of opening up these condensed systems is by the admixture of other molecules possessing residual affinity, that is to say, molecules in which the opposite types of affinity are not balanced, so that after the maximum condensation possible has taken place there is left over a residue. The lines of force due to this residual affinity will interpenetrate the closed systems of the unreactive molecules, with the result that they will become opened partly or wholly, and they will develop chemical reactivity towards other similarly-opened systems. For this reason the extraordinary influence of water-vapour in causing the above pairs of substances to unite together may be understood.

Again, it appears that light waves also are able in many cases to open the closed systems, for we have definite evidence that many chemical reactions, such as, for example, the union of hydrogen and chlorine, are catalysed by the light rays. Inasmuch as the light in opening the system is doing work against chemical forces, this gives us a rational explanation of the selective absorption of light.

A point of some considerable interest may be noted in connexion with the closed field of force surrounding a complex molecule. It is evident that in such a case as this the potential gradient within the closed field will be complex, and the tendency will be for the solvent or the light waves to attack that portion of the system where the potential gradient is the steepest. This at once suggests the fact that a complicated system such as must surround the more complex molecules will be opened in stages, and on this conception was based a theory of fluorescence, and some definite evidence was brought forward in strong support of it.

Although, as has been pointed out, light waves have the power of opening the systems, it does not necessarily follow that light alone should always be able to open a system, especially if the substance in question is in the absolutely pure state. On the other hand, such substances as are very little affected by light rays in the pure state may have their systems sufficiently opened by means of a solvent for the light rays to act on them and to open their systems still further. This point is capable of direct observation, because it is perfectly possible to measure quantitatively the amount of light absorbed by a given quantity of a substance, both in the pure state and also in solution in some diactic solvent. It is evident that if the closed system of a substance were opened up by means of solution in some solvent, the quantity of light absorbed by the substance in the pure state and in solution would be different. In fact, this would afford a reasonable explanation of the progressive variation that has so frequently been observed from Beer's law. It would follow from the conception here put forward that in the case of a substance, the closed field of force of which is opened by a solvent, the amount of light absorbed should increase with the dilution, provided, of course, that the thickness of the solution were comparable. In the ideal case one would expect the following series of phenomena to be realised. If the quantity of light absorbed by a given thickness of the pure substance were measured, then, according to Beer's law, this quantity should also be absorbed by double the thickness of a solution in some diactic solvent of that substance with a concentration of 50 per cent., and so on. On the other hand, if the solvent tends to open the closed force fields of the substance in question, then the absorption of the solution will be greater than that of the pure substance. Further, the absorption should increase with further dilution until a maximum is reached. If the dilution be still further increased, the absorption should then diminish until it finally vanishes. It must clearly be understood that this series of phenomena can only be observed if a single simple condition of

opening up the closed field of force comes into play. If on increasing the dilution a second stage of the opening up is involved, it is manifest that the above quantitative relations will not hold.

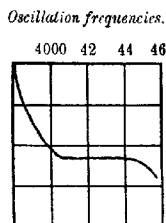
We have made several quantitative investigations of the amount of light absorbed, and we find that the facts observed are very similar to those which the theory led us to expect.

Strictly speaking, such observations as these should be made by means of a spectrophotometer, but as our observations dealt with ultraviolet absorption it was not found possible to devise a satisfactory spectrophotometer for this purpose. The substance most completely investigated by us was ethyl acetoacetate, the absorption curve of which is shown in the figure, and although we were not able to make direct spectrophotometric measurements, yet it is evident that the height on the ordinate at which the step-out on the absorption curve appears will give a relative measure of the amount of light absorbed. In other words, by comparing together these heights obtained under different conditions of

solution we were able to observe these thicknesses of material which just allowed the light to pass through, and these thicknesses at once give a quantitative relation of the amount of light absorbed. It will be understood that this will depend entirely on the constancy of the source of light used, for if any variation takes place in the intensity of the source of light used it is evident that inaccurate values will at once be obtained. The source of light used in our experiments was the electric spark between carbon poles which had been boiled successively in concentrated solutions of uranium nitrate and ammonium molybdate and heated to redness after each such treatment.

In using this source it was found that exceedingly constant results were obtained. A further point of difficulty was at first met with in the developing of the photographic plates after exposure, but this was readily overcome by always using the same strength of developer and leaving the plates in this solution for the same time in every case. We then had little difficulty in obtaining perfectly constant results. In order to ensure the greatest accuracy, as many comparative exposures as possible were taken on the same plate, so that every one of these was subject to the same conditions in development.

In the measurements of the absorption of the pure substances and their concentrated solutions it was, of course, necessary to use very thin layers, and for this purpose a special cell was designed



and made for us by Hilger, somewhat resembling that used by Purvis in his work on the absorption of pure substances. The cell consists of two quartz plates, which are similar to those used in the Perot and Fabry interferometer. Each plate is about 10 mm. thick, and whilst one is mounted on a rigidly fixed stand, the other is mounted on a very accurate micrometer screw, so that the distance between the two can be adjusted. The micrometer screw is provided with a vernier by means of which the distance between the plates can be read to 0.001 mm., and the whole mounting is very massive, so that there is little danger of displacement when very thin films of liquid are employed owing to the pressure due to surface tensions.

Before any experiments were done the zero of the instrument was checked by bringing the two quartz plates as close together as possible, and observing the set of interference fringes produced by the air layer between them.

It has already been said that the relative amounts of light absorbed by the substance under investigation were obtained by a comparison of the thickness through which the light rays corresponding with the absorption band were just transmitted, for example, in the case of ethyl acetoacetate a $N/2000$ -solution in alcohol, this transmission just took place at a thickness of 30 mm., that is, in plotting the absorption curve of a $N/2000$ -solution the head of the absorption band was found at 30 mm.; at $N/1000$ -concentrations this step-out was found with a thickness of 15 mm. With $N/200$ - or $N/20$ -solutions the thicknesses at which the step-out occurred were 0.3 mm. and 3 mm. respectively.

It will be seen that these thicknesses are inversely proportional to the concentration, and therefore over this range of concentration Beer's law holds good. On the other hand, in the case of a $N/2$ -solution the thickness at which the step-out occurred was found to be 0.05 mm., when, of course, from Beer's law it ought to be 0.03 mm. In the case of the $N/2$ -solution, therefore, less light is absorbed than would be expected from Beer's law, because a greater thickness of that solution is necessary to produce a given absorption than that calculated from Beer's law. With increasing concentrations the divergence from Beer's law is still further marked, and in the case of the pure substance this divergence is very great indeed.

The complete set of observations are contained in table I, in which the first column contains the molecular concentration of the material. The second column shows the actual observed thicknesses through which the light of the absorption band is just transmitted, and in the third column are the thicknesses calculated from Beer's

law. In the fourth column are shown the differences between the observed and calculated values, whilst the fifth column contains the ratios of these differences to the calculated thickness.

The greatest concentration obtainable, of course, was the pure substance itself, which was approximately $7.923N$. On attempting to examine a still greater dilution than $N/2000$ in alcohol, it was found impossible to obtain accurate measurements owing to the fact that with the long length then necessary the absorption exerted by the alcohol came into play.

This, however, does not hold good in the case of water, because pure distilled water is quite diatonic up to very long lengths. We therefore investigated aqueous solutions of ethyl acetoacetate, starting with the most concentrated solution which could conveniently be managed in this solvent, which was $N/20$. It was noticed at once that the absorptive power of the aqueous solution is very much less than that of the alcohol solution of the same concentration, but this, of course, does not prevent any comparisons being made between any set of observations taken with the same solution. In table II are shown the results obtained with some aqueous solutions of ethyl acetoacetate, and it will be seen that in the case of the first two, Beer's law holds good. In the case of the $N/500$ -solution the absorption is distinctly less than Beer's law would lead us to expect, and in the case of the $N/1000$ -solution the selective absorption has entirely disappeared.

These results seem to us to be of considerable interest, for, although the same solvent has not been used throughout, it is quite evident that, starting from the pure substance, an increase in the amount of solvent present first of all causes a progressive increase in the amount of light absorbed until a constant maximum is reached. Further dilution then causes a decrease in the absorption, which is followed by an entire disappearance of the selective absorption.

Inasmuch as this result is exactly that prophesied by the general theory advanced above, we feel that it may be regarded as affording very great support to the theory.

In case it may be urged that the disappearance of the selective absorption in the case of the aqueous solution is due to the ionisation of the ester, it may be pointed out that a $N/1000$ -solution in water at which the concentration of the selective absorption has disappeared, only about 0.1 per cent. of the ester is ionised.

We have also examined pyridine, and find somewhat similar results, although we have not yet been able to reach the dilution at which the pyridine ceases selectively to absorb light. In table III are shown the results given by pyridine, water being used as a

solvent. From this statement it will be seen that a constant maximum is not reached before $N/50$ -concentration, and that the deviation from Beer's law with greater concentrations is even more strikingly marked than in the case of ethyl acetoacetate. The first set of observations in the table refer to pure pyridine, which is about $12.4N$. It may be pointed out that pyridine exhibits a very well-marked and deep absorption band, and the thicknesses given in table III refer to those thicknesses through which the rays of light correspond with the absorption band are just transmitted, that is, they refer to those thicknesses at which the head of the absorption band is observed.

We would draw attention to the fact that we find some divergence between our observations and some given by Purvis; for example, Purvis (T., 1910, 97, 1546) states that no selective absorption is shown by films of aniline, even when the thickness is reduced to 0.001 mm. We find, however, clear evidence of the well-known absorption band, which, indeed, extends over a range of 0.015 to 0.009 mm.

It seems only reasonable to conclude from this that the thicknesses which Purvis gives in his papers are wrong. We would

TABLE I.

Ethyl Acetoacetate and Alcohol.

Normality.	Observed thickness.	Calculated thickness,	Difference, obs.—calc.,	<i>b/a</i> .
		<i>a</i> .	<i>b</i> .	
	mm.	mm.	mm.	
7.923	0.016	0.001893	0.015107	7.4
5.0	0.020	0.003	0.017	5.7
2.0	0.028	0.0075	0.0205	2.7
1.0	0.037	0.015	0.022	1.5
0.5	0.05	0.03	0.02	0.7
0.1	0.15	0.15	0	0
0.05	0.3	0.3	0	0
0.005	3.0	3.0	0	0
0.0025	6.0	6.0	0	0
0.00125	12.0	12.0	0	0
0.001	15.0	15.0	0	0
0.0005	30.0	30.0	0	0

TABLE II.

Ethyl Acetoacetate and Water.

Normality.	Observed thickness.	Calculated thickness,	Difference, obs.—calc.,	<i>b/a</i> .
		<i>a</i> .	<i>b</i> .	
	mm.	mm.	mm.	
0.05	6	6	0	0
0.025	12	12	0	0
0.01	25	30	-5	-0.17
0.002	120	150	-30	-0.2
0.001	Selective absorption ceased			

TABLE III.
Pyridine and Water.

Normality.	Observed thickness.	Calculated thickness,	Difference, obs.—calc.	<i>b/a</i> .
		<i>a</i> .	<i>b</i> .	
	mm.	mm.	mm.	
12.4	0.010	0.00064	0.00936	14.7
10.0	0.011	0.0008	0.0102	12.7
7.0	0.013	0.00114	0.01186	10.4
5.0	0.014	0.0016	0.0124	7.7
4.0	0.015	0.002	0.0130	6.5
2.0	0.019	0.004	0.015	3.7
1.0	0.024	0.008	0.016	2.0
0.2	0.067	0.04	0.027	0.67
0.02	0.40	0.40	0	0
0.002	4.0	4.0	0	0
0.0002	40.0	40.0	0	0

suggest that the mounting of the quartz plates in his cell is not sufficiently rigid to stand the strain produced by surface tension of the very thin films. If this were so when the plates are brought close together with a thin film of liquid in between them, the readings given by the instrument are very much smaller than the real thickness of the film owing to the fact that the plates have been forced apart by the surface tension. We would point out that if our instrument, even much more rigid though it be than that used by Purvis, is subject to the same error in a less degree, then such an error would tend to decrease the deviation that we have observed from Beer's law. In other words, if our readings are subject to a correction from this cause, such a correction would increase the deviations which we have observed.

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XIV.—*The Constitution of Cytisine, the Alkaloid of Cytisus Laburnum. Part I. The Synthesis of α-Cytisolidine and of β-Cytisolidine.**

By ARTHUR JAMES EWINS.

CYTISINE, the poisonous alkaloid of the common laburnum (*Cytisus laburnum*), was first isolated in a pure state by Husemann and Marmé (*Zeitsch. f. Chem.*, 1865, 1, 161), who gave it the formula $C_{20}H_{27}ON_3$. Partheil (*Ber.*, 1890, 23, 3201), however, showed the true composition of the alkaloid to be $C_{11}H_{14}ON_2$, and

* This communication forms part of an investigation which is being carried out in collaboration with Dr. G. Barger.

this formula was confirmed by Buchka and Magelhaës (*Ber.*, 1891, **24**, 273, 674), as well as by subsequent workers.

The alkaloid is present in many other plants, for example, in other kinds of cytisus and in *Ulex europæus*, the common gorse, the "ulexine" of which, isolated by Gerrard (*Ber.*, 1886, **19**, 838), was shown by Partheil and others to be identical with cytisine.

The interest attaching to this alkaloid has been very considerably increased by the recent work of Dale and Laidlaw (*J. Pharm. Expt. Ther.*, 1912, **3**, 205), who have shown that its physiological action is in all respects qualitatively and almost quantitatively indistinguishable from that of the very poisonous alkaloid nicotine. The question of its chemical constitution accordingly becomes of interest in so far as one might perhaps expect some chemical relationship with that of the latter alkaloid.

The chemical constitution of cytisine has previously been worked at chiefly by two investigators: Partheil (*loc. cit.*), and more especially by M. Freund and his co-workers (*Ber.*, 1901, **34**, 615; 1904, **37**, 16; 1906, **39**, 814). To the latter the following main facts with regard to the alkaloid are due. On treatment with hydriodic acid and phosphorus at a high temperature (230°) the alkaloid is decomposed, yielding as the main products of the reaction the following substances:

(a) Cytisoline, $C_{11}H_{11}ON$, a feebly basic, crystalline solid, melting when pure at 198°.

(b) β -Cytisolidine, $C_{11}H_{15}N$ (Freund), a basic oil, yielding a crystalline picrate (m. p. 229°) and platinichloride (m. p. 234°).

(c) A mixture of hydrocarbons melting at 185–230°.

(d) Ammonia.

Of these products, cytisoline on reduction with sodium and alcohol gives a base, α -cytisolidine, $C_{11}H_{16}N$, considered by Freund to be isomeric with β -cytisolidine. This base yielded an oily picrate and a crystalline platinichloride melting at 216°. Further, cytisoline on oxidation with chromic acid gives an acid, cytisolinic acid, $C_{10}H_8ON(CO_2H)$, obviously by oxidation of a methyl group in the molecule.

Lastly, Freund (*Ber.*, 1904, **37**, 16; 1906, **39**, 814) showed that on electrolytic reduction, cytisine, $C_{11}H_{14}ON_2$, was converted into a base, tetrahydrodeoxycytisine, $C_{11}H_{20}N_2$. Experiments soon showed that the main hope of gaining any further knowledge of the constitution of the alkaloid lay in the elucidation of the constitution of the products obtained by Freund by the action of hydriodic acid. Many attempts were made to obtain some product of oxidation from cytisine which would throw some light on the problem of its constitution. Cytisine is very readily attacked by oxidising agents,

such as potassium permanganate and chromic acid, but, however the conditions of oxidation were varied, no pure product could be isolated except oxalic acid.

Equally disappointing were the attempts which were made to decompose the alkaloid by the action of acids or alkalis at high temperatures. Towards these reagents cytisine is stable to a remarkable degree. After heating with concentrated or dilute sulphuric or hydrochloric acids to temperatures of from 200° to 250°, or higher, for some time, the greater part of the alkaloid was recovered unchanged. Only with a saturated solution of hydrogen bromide in acetic acid, at a temperature of 250°, was there any indication of the formation of a new crystalline derivative, and even in this case the yield was extremely small. These experiments were consequently abandoned.

In repeating the experiments of Freund it was noticed that the base α -cytisolidine, obtained by the reduction of cytisoline by the action of sodium in alcohol, when dissolved in sulphuric acid and treated with a drop of nitric acid, gave a carmine-red colour shading to blue at the edge of the liquid. This reaction is somewhat similar to that given by tetrahydroquinoline, and it was considered probable that α -cytisolidine might be a substituted tetrahydroquinoline. Freund himself had considered the possibility of its being 1:8-dimethyltetrahydroquinoline, but synthesis of the latter compound had shown that this was not the case (*Ber.*, 1904, 37, 22). The absence of a methyl group attached to the nitrogen atom of the base was easily shown, since a determination carried out according to the method of Herzig and Meyer for such a grouping gave a negative result. Moreover, since cytisoline has been shown to contain a methyl group, it follows that α -cytisolidine must be a dimethyltetrahydroquinoline if it is indeed a derivative of tetrahydroquinoline, and cytisoline a hydroxydimethylquinoline. The general properties of cytisoline gave considerable support to the above hypothesis when compared with those of the corresponding hydroxyquinolines already described in the literature. Like these derivatives, cytisoline is a feeble base. Its salts are dissociated by water, it gives a brownish-red coloration with ferric chloride solution, and on reduction it loses oxygen, taking up four atoms of hydrogen to give a base volatile in steam.

Excluding the bases containing a methyl group attached to the nitrogen atom, there are possible twenty-one isomeric dimethyltetrahydroquinolines. Of these, some ten are mentioned in the literature, but few of these are by any means well characterised. The task of identifying the base was therefore no light one. The synthesis of what were considered to be the more likely of these

dimethyltetrahydroquinolines was commenced in collaboration with Mr. H. King, and some of the results of this work are described in the succeeding paper (Ewins and King, p. 104).

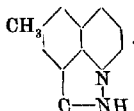
The work carried out in this direction unexpectedly threw a further light on the relationship of α -cytisolidine to β -cytisolidine, the basic oil obtained by the action of hydriodic acid on cytisine. The last-mentioned authors found a well-marked and fairly constant difference in the properties of the dimethyltetrahydroquinolines and the corresponding dimethylquinolines, chiefly in the melting points and solubilities of their salts. A similar relationship was observed to exist between the α - and β -cytisolidines, and a closer examination and analysis showed that the latter possessed the composition $C_{11}H_{11}N$, and not $C_{11}H_{13}N$, as stated by Freund (*loc. cit.*). It was therefore very probable that α -cytisolidine was the dimethyltetrahydroquinoline corresponding with the dimethylquinoline, β -cytisolidine, a relationship which was readily confirmed, β -cytisolidine on reduction with sodium in alcoholic solution giving a base identical with α -cytisolidine.

The problem thus resolved itself into the identification of β -cytisolidine as (probably) a dimethylquinoline. Here, again, there are twenty-one possible isomerides, of which about a dozen have been described, but again for the most part very imperfectly.

Finally, after a number of these dimethylquinolines had been prepared, the synthesis of 6:8-dimethylquinoline from *m*-4-xylydine was carried out. The base so obtained proved to be identical with β -cytisolidine, and on reduction yielded another base identical with α -cytisolidine. The constitution of these two bases is thus established beyond doubt. Further, cytisoline must be a corresponding hydroxydimethylquinoline. This is confirmed by the fact that on distillation with zinc dust β -cytisolidine is obtained. The position of the hydroxy-group is, however, as yet undetermined; but it is most probably either in the 3- or 4-position, since 2-hydroxy-6:8-dimethylquinoline prepared by the action of hypochlorous acid on 6:8-dimethylquinoline, although agreeing closely in general properties with cytisoline, was found to be different. 5-Hydroxy-6:8-dimethylquinoline was also synthesised, but the properties of this substance differ considerably from cytisoline, owing to the phenolic character of the hydroxy-group, for which reason also 7-hydroxy-6:8-dimethylquinoline may most probably be eliminated. Experiments to determine the constitution of cytisoline are in progress.

The constitution of cytisine itself still remains an open question. It is to be noticed, however, that cytisoline, $C_{11}H_{11}ON$, which, from the results recorded in this communication, must be a hydroxydimethylquinoline, is formed from cytisine by the loss of the elements

of ammonia alone. The manner in which this elimination takes place is at present quite unknown. The most simple explanation is perhaps that cytosine is formed by the fusion of three rings (benzene, pyridine, and pyrazole rings), somewhat according to the following scheme:



Such a compound might conceivably lose ammonia under the conditions described, to yield dimethylquinoline derivatives; but there is so far no direct evidence in support of such a structure.

EXPERIMENTAL.

The Action of Hydriodic Acid and Phosphorus on Cytisine.

The method employed by Freund (*Ber.*, 1904, 37, 16) to obtain cytosoline was as follows: Two grams of cytosine, 1 gram of red phosphorus, and 10 c.c. of hydriodic acid (D 1.7) were heated in sealed tubes for four hours at 225–230°. In this way 5 grams of cytosoline were obtained from 40 grams of cytosine. Experiment confirmed these results, but a slight modification was adopted by which the yield was somewhat increased. This consisted in heating 2 grams of cytosine, 0.4 gram of phosphorus, and 4 c.c. only of hydriodic acid to 230–235° for three hours. In this way, an average yield of 3.5 grams of cytosoline (m. p. 180°) was obtained from 20 grams of cytosine. At a slightly lower temperature a somewhat less pure product was obtained consisting of cytosoline, together with a substance or substances possessing very similar properties which render purification a matter of considerable difficulty. The reaction product was treated in a manner somewhat different from that employed by Freund. The contents of the tubes were poured into water, and on keeping the crystalline cytosoline separated out and was collected. The acid filtrate, on neutralisation, yielded a further small quantity of cytosoline. The solution was finally rendered alkaline with sodium hydroxide and distilled in a current of steam, when β -cytosolidine, together with a little α -cytosolidine, passed over. The yield of the base was small. From the residue in the distilling flask a considerable amount of unchanged cytosine could be recovered by extraction with chloroform.

The Formation of β -Cytisolidine from Cytisoline by Distillation with Zinc Dust.

Four grams of cytisoline were distilled over zinc dust and zinc pumice in a current of hydrogen at a dull red heat. The red, oily distillate was dissolved in dilute (5 per cent.) hydrochloric acid, and the filtered acid solution extracted with ether. The small amount of extracted material was discarded. The aqueous solution was then rendered alkaline with sodium hydroxide, and again extracted with ether. The ethereal solution was washed with water, dried over anhydrous potassium carbonate, and the ether evaporated. The residue was distilled, and 0.9 gram of a colourless, limpid oil boiling at 132–133°/14 mm. was obtained. This base was easily shown to be identical with β -cytisolidine by comparison of its salts. The identity is shown in the following table:

	Base from cytisoline.	β -Cytisolidine.
Picrate.....	224°	224–225° (Freund 226°)
Platinichloride	234–235	234–235
Nitro-derivative.....	104	104–105

The melting points of mixtures in all these cases showed no depression.

The Synthesis of β -Cytisolidine (6:8-Dimethylquinoline).

6:8-Dimethylquinoline was originally obtained by Leeds (*Ber.*, 1873, **16**, 289) by the dry distillation of xylidineacrolein, and was by him termed kryptidin. It was then obtained by Berend (*Ber.*, 1874, **17**, 2716) from *m*-4-xylidine by the Skraup synthesis.

For the preparation of the base the latter method was employed. Ten grams of *m*-4-xylidine, 5 grams of nitrobenzene, and 24 grams of glycerol were heated together in a large flask on a sand-bath, and 20 grams of concentrated sulphuric acid were gradually run through a dropping funnel into the heated mixture. In this way the reaction proceeded quite smoothly. The product was worked up in the usual manner, and 6.5 grams of a base boiling at 133–134°/14 mm. were obtained. (Found, C=83.9; H=7.1. Calc., C=84.0; H=7.0 per cent.)

The identity of this base with cytisolidine is shown by the following table:

	6:8-Dimethylquinoline.	β -Cytisolidine.
Boiling point.....	133–134°/14 mm.	132–133°/14 mm.
Picrate.....	221–224	224–225 (Freund 226°)
Platinichloride	234–235	234–235
Hydrochloride	246	250–260
Nitro-derivative.....	105	104–105

Mixed melting points in all cases showed no depression.

The formula $C_{11}H_{15}N$ assigned by Freund (*loc. cit.*) to β -cytisolidine was thus shown to be inaccurate. A specimen of β -cytisolidine picrate melting at $224-225^\circ$, obtained from cytisine by the action of hydriodic acid, was analysed with the following result:

0.1038 gave 0.2024 CO_2 and 0.0354 H_2O . $C=53.2$; $H=3.8$.

$C_{11}H_{15}N, C_6H_3O_7N_3$ requires $C=52.8$; $H=3.6$ per cent.

The Synthesis of α -Cytisolidine (6:8-Dimethyl-1:2:3:4-tetrahydroquinoline).

Three grams of 6:8-dimethylquinoline were reduced in alcoholic solution with 5 grams of sodium. The mixture was diluted with water, the alcohol evaporated off, and the residue distilled in a current of steam. The distillate was extracted with ether, the ethereal solution washed and dried in the usual way, and the residue after evaporation of the ether distilled under diminished pressure. There were thus obtained 2.1 grams of a liquid boiling at $137^\circ/11$ mm.:

0.1582 gave 0.4746 CO_2 and 0.1328 H_2O . $C=81.8$; $H=9.3$.

$C_{11}H_{15}N$ requires $C=82.0$; $H=9.3$ per cent.

This was proved to be identical with α -cytisolidine by the preparation of a number of salts and derivatives, as shown by the following table:

	6:8-Dimethyl- 1:2:3:4-tetra- hydroquinoline.	α -Cytisolidine.	
		Freund.	Ewins.
Boiling point	$137^\circ/11$ mm.	—	$141-142^\circ/14$ mm.
Picrate	$147-148$	—	146
Platinichloride	$214-215$	oily	214—215
Iodide of methyl derivative..	166	216°	$164-165$
Benzoyl derivative	103	—	103

Melting points of mixtures in all cases showed no depression.

Since 6:8-dimethyl-1:2:3:4-tetrahydroquinoline has not previously been synthesised, a more detailed account of its salts and derivatives follows.

The *picrate* is best prepared by the addition of an ethereal solution of picric acid to an ethereal solution of the base. The salt is not immediately precipitated, but on addition of light petroleum and rubbing with a glass rod, a gummy, reddish-yellow solid separates, which gradually hardens, and can then be collected. It is best crystallised from benzene by careful addition of light petroleum, when it separates in large, orange-yellow, rhombic plates, melting at $147-148^\circ$.

In the presence of water this salt shows a very great tendency

to separate as an oil. Freund's failure to crystallise this salt is probably explained by this fact.

The *benzoyl* derivative is readily prepared by the Schotten-Baumann reaction, and crystallises from dilute alcohol in prisms melting at 103°:

0.1468 gave 0.4358 CO₂ and 0.0922 H₂O. C=81.0; H=7.0.

C₁₈H₁₆ON requires C=81.5; H=7.2 per cent.

1:6:8-Trimethyl-1:2:3:4-tetrahydroquinoline *Hydriodide*.

This salt is produced by the addition of one molecule of methyl iodide to 6:8-dimethyl-1:2:3:4-tetrahydroquinoline.

6:8-Dimethyl-1:2:3:4-tetrahydroquinoline (0.4 gram) was boiled for a few minutes with a slight excess of methyl iodide. The solution was evaporated to dryness, the residue dissolved in a little methyl alcohol, and dry ether added, just insufficient to produce a precipitate. On keeping, crystals of the above salt separated out. They formed prisms melting at 164—165° (0.26 gram):

0.1242 gave 0.2156 CO₂ and 0.0638 H₂O. C=47.4; H=5.7.

C₁₂H₁₇N.HI requires C=47.5; H=5.9 per cent.

THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
HERNE HILL, S.E.

XV.—The Synthesis of Some New Dimethyltetrahydroquinolines.

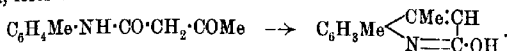
By ARTHUR JAMES EWINS and HAROLD KING.

In the course of an investigation which is being carried out by one of us in conjunction with Dr. G. Barger, it became necessary for the purpose of comparison to prepare certain hydroxydimethylquinolines and their reduction products. Reference to the literature showed that a number of such substituted hydroxyquinolines had already been prepared, chiefly by Knorr (*Ber.*, 1884, 17, 542; *Annalen*, 1889, 245, 358) and Conrad and Limpach (*Ber.*, 1888, 21, 525).

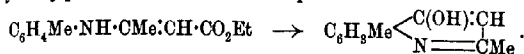
In the first place, we attempted the preparation of 2-hydroxy-4:8-dimethylquinoline by Knorr's method. This consists in heating molecular proportions of *o*-toluidine and ethyl acetoacetate in sealed tubes at 150—160° for several hours, and subsequently treating the crude product with cold concentrated sulphuric acid. On pouring into water, the hydroxyquinoline is precipitated. The method,

however, gave very unsatisfactory results, a poor yield of an obviously very impure product being obtained. We subsequently found that the product described by Knorr as 2-hydroxy-4:8-dimethylquinoline must also have been very impure, since he gives for this compound a melting point of 185°, whereas we find that the pure substance melts at 217°.

The formation of a hydroxyquinoline by the above process depends on the production of the toluidide of acetoacetic acid, which then, under the dehydrating action of concentrated sulphuric acid, loses water as follows:



The intermediate toluidide was not isolated by Knorr. Pawlewski (*Ber.*, 1889, **22**, 2203), however, described a substance obtained from the product, which he considered to be β -tolyliminocrotonic acid (isomeric with the toluidide), in accordance with Knorr's original view (*Ber.*, 1884, **17**, 542) that condensation took place, not as indicated above, but according to the following scheme, whereby 4-hydroxyquinoline derivatives were produced:



Knorr, however, had already corrected his original interpretation of the reaction, and Pawlewski's substance was in all probability, from its melting point and the analytical figures, the *o*-toluidide of acetoacetic acid. The 4-hydroxyquinolines were afterwards synthesised by Conrad and Limpach from the β -toluidinocrotonic esters obtained by the interaction of the substances in the cold (*Ber.*, 1888, **21**, 525).

As we required considerable quantities of these hydroxyquinolines for our purpose, we experimented with the object of obtaining the required toluidides in a state of purity and improved yield. After several attempts we found that by simply boiling together molecular proportions of the necessary toluidine and ethyl acetoacetate for a very short time (one to one and a-half minutes) the product solidified on cooling to a mass of crystals, which, after recrystallisation, were obtained pure in good yield, averaging 55 per cent. of the theoretical.* The toluidides so obtained are readily and almost quantitatively converted into the corresponding hydroxyquinolines (carbostyrile) by heating at 100° for ten to fifteen minutes with concentrated sulphuric acid. On pouring into water, the hydroxyquinolines separate out immediately in an almost pure condition.

The hydroxyquinolines so obtained on reduction with sodium

* The preparation of the anilide of ethyl acetoacetate can be readily carried out in a precisely similar manner.

and alcohol are converted mainly into the corresponding tetrahydroquinolines. There are indications of the formation of intermediate products, possibly hydroxydihydroquinolines, but this has not so far been investigated. On distillation with zinc dust, the hydroxyquinolines are converted into dimethylquinolines (Knorr, *Annalen*, 1889, **245**, 358). The reduction, however, takes place only with some difficulty, a rather high temperature and a current of hydrogen being essential in order to obtain a satisfactory yield of base. The characterisation of these dimethylquinolines as at present recorded is very unsatisfactory and incomplete. We have accordingly redetermined the boiling points of these bases, and place on record some of their more characteristic salts and derivatives.

The new dimethyltetrahydroquinolines described in this communication are readily distinguished from the corresponding dimethylquinolines by the following properties. Whilst the dimethylquinolines give no coloration when dissolved in sulphuric acid (the solution, however, shows a marked blue fluorescence) and treated with a drop of nitric acid, with the tetrahydro-derivatives well-marked colour reactions are obtained. Again, the salts of the tetrahydro-bases generally melt at a considerably lower temperature than those of the dimethylquinolines, the picrates, for example, differing by about 60—70°. The picrates of the tetrahydro-bases are orange or orange-yellow salts, moderately soluble in water, and very readily so in acetone. Those of the dimethylquinolines are pale yellow, and very sparingly soluble in hot water or alcohol. The tetrahydro-bases also yield characteristic benzoyl derivatives of low melting point by the Schotten-Baumann reaction.

EXPERIMENTAL.

Acetoaceto-o-toluidide, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{Me}$.

A mixture of 30 grams of ethyl acetoacetate and 24 grams of *o*-toluidine was rapidly heated to boiling, and the liquid kept vigorously boiling for one to one and a-half minutes. The cooled product set to a mass of crystals, which were collected and recrystallised from ethyl acetate, when short, rectangular prisms (25 grams) melting at 107—108° were obtained:

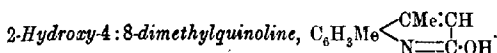
0.1562 gave 0.3943 CO_2 and 0.1008 H_2O . $\text{C}=68.8$; $\text{H}=7.2$.

0.1950 „ 12.5 c.c. N_2 (moist) at 10° and 760 mm. $\text{N}=7.6$.

$\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C}=69.1$; $\text{H}=6.8$; $\text{N}=7.3$ per cent.

We were also able to isolate a certain amount of this toluidide from the reaction product obtained by Knorr's method (heating to 150—160° in sealed tubes), and it is most probable that the

substance isolated by Pawlewski (*Ber.*, 1889, **22**, 2203) from this reaction product, and considered by him to be *o*-tolyliminocrotonic acid (m. p. 111—112°), was, in fact, acetoaceto-*o*-toluidide. Since, however, no details of the method of isolation or of the properties of the substance are given, it is not possible to determine this point except by synthesis of the acid. That the toluidide possesses the constitution assigned to it by the present authors is obvious from the fact that the product is insoluble in sodium carbonate, showing the absence of the carboxyl group, and that the alcoholic solution gives with ferric chloride a purple coloration indicative of the enolic form of the acetoacetic grouping which could hardly be the case if the substituting toluidine were in the position assigned to it by Pawlewski. Its constitution further follows from its ready conversion into 2-hydroxy-4:8-dimethylquinoline by the action of dehydrating agents, whereas the acid described by Pawlewski would be expected to give the isomeric 4-hydroxy-2:8-dimethylquinoline obtained by Conrad and Limpach by another method.

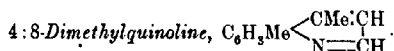


Acetoaceto-*o*-toluidide (19 grams) was dissolved in concentrated sulphuric acid (20 c.c.), and the mixture heated in the boiling-water bath for fifteen minutes. The product was then poured into about ten volumes of water, when a white, crystalline solid separated. After some time this was collected, and recrystallised from dilute acetic acid, when it separated in long, thin plates, melting at 217—218°:

0.1180 gave 0.3310 CO₂ and 0.0628 H₂O. C=76.5; H=5.9.

C₁₁H₁₁ON requires C=76.3; H=6.3 per cent.

This carbostyryl was originally described by Knorr (*Ber.*, 1884, **17**, 542), who obtained it in a very impure form, melting at 185° from the crude product obtained as described. The substance is a weak base, very sparingly soluble in cold water, more readily so in hot. It forms salts with concentrated mineral acids, but these are decomposed by excess of water with liberation of the crystalline base. On distillation with zinc dust it yields 4:8-dimethylquinoline, and on reduction by sodium and alcohol, 4:8-dimethyl-1:2:3:4-tetrahydroquinoline.



This base was originally described by Knorr as a pungent oil boiling at 273—274°/751 mm. It is obtained by distilling

2-hydroxy-4:8-dimethylquinoline over zinc dust in a current of hydrogen. In order to purify the base it was converted into the pure picrate described below. The salt so obtained was treated with a concentrated solution of potassium hydroxide, and distilled in a current of steam. The oily liquid was extracted from the distillate by means of ether, and, after drying and removal of the solvent, distilled. The base was an almost colourless, limpid oil, boiling at 134—135°/12 mm. and 258—259°/758 mm., which on keeping solidified to a crystalline mass melting at 54—55°. (Found, C=83.5; H=7.0. $C_{11}H_{11}N$ requires C=84.0; H=7.0 per cent.)

4:8-Dimethylquinoline picrate was obtained by precipitating the ethereal solution of the base by an ethereal solution of picric acid. The salt was recrystallised from dilute alcohol, and was obtained in lemon-yellow, rhombic prisms, melting at 216—217°:

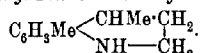
0.1821 gave 0.3506 CO_2 and 0.0582 H_2O . C=52.6; H=3.5.

$C_{11}H_{11}N \cdot C_6H_3O_7N_3$ requires C=52.8; H=3.6 per cent.

The salt is very sparingly soluble in hot water or alcohol, but rather more readily so in acetone.

The *platinichloride* crystallises from dilute alcohol in buff-coloured needles, melting and decomposing at 226—227° (Knoorr gives 220°).

4:8-Dimethyl-1:2:3:4-tetrahydroquinoline,



2-Hydroxy-4:8-dimethylquinoline (7.5 grams) was reduced by sodium (15 grams) in concentrated absolute alcoholic solution. The solution was diluted with an equal volume of water, the alcohol distilled off, and the residue distilled in a current of steam. The oily liquid which passed over was extracted with ether, the ethereal solution dried over potassium carbonate, and after evaporating off the ether the residue was fractionally distilled. The distillate was converted into the picrate, which was obtained pure by recrystallising from dilute alcohol. The regenerated base then boiled at 133—134°/16 mm. and at 256—258°/750 mm.:

0.1566 gave 0.4708 CO_2 and 0.1322 H_2O . C=82.0; H=9.4.

$C_{11}H_{15}N$ requires C=82.0; H=9.3 per cent.

4:8-Dimethyl-1:2:3:4-tetrahydroquinoline is a colourless oil, very sparingly soluble in water, and easily volatile with steam. When treated with concentrated sulphuric acid and a drop of nitric acid a deep orange-red colour is produced.

The *picrate*, obtained in the usual manner, forms orange-yellow,

rhombic prisms, melting at 160° . It is sparingly soluble in cold water, but fairly readily so in hot water, alcohol, or acetone:

0.1090 gave 0.2096 CO_2 and 0.0448 H_2O . $\text{C}=52.4$; $\text{H}=4.6$.

$\text{C}_{11}\text{H}_{15}\text{N}_3\text{C}_6\text{H}_5\text{O}_7\text{N}_3$ requires $\text{C}=52.3$; $\text{H}=4.6$ per cent.

The *benzoyl* derivative, $\text{C}_{18}\text{H}_{19}\text{ON}$, prepared by the Schotten-Baumann reaction, crystallises from dilute alcohol in prisms melting at $104-105^{\circ}$.

Acetoaceto-m-toluidide, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$.

This compound is obtained by a method exactly similar to that employed in the preparation of the ortho-compound. On recrystallisation from benzene and light petroleum it separated in pearly leaflets melting at $57-58^{\circ}$:

0.1570 gave 0.3972 CO_2 and 0.0980 H_2O . $\text{C}=69.0$; $\text{H}=6.93$.

$\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C}=69.1$; $\text{H}=6.8$ per cent.

Its general properties are in all respects similar to those of the isomeric ortho-compound.

Owing to the low melting point of the solid, however, its separation from the crude product was found to be somewhat troublesome. In the preparation of the corresponding 2-hydroxy-4:7-dimethylquinoline, therefore, the crude product was directly treated with concentrated sulphuric acid at 100° for fifteen minutes, and the product poured into water. After crystallisation from dilute acetic acid a good yield (41 per cent.) of the hydroxyquinoline melting at 220° was readily obtained. From this the corresponding 4:7-dimethylquinoline and 4:7-dimethyl-1:2:3:4-tetrahydroquinoline were obtained by zinc dust distillation and reduction by sodium in alcohol respectively.

4:7-Dimethylquinoline, $\text{C}_{11}\text{H}_{11}\text{N}$.

2-Hydroxy-4:7-dimethylquinoline was distilled with zinc dust as described in the case of the corresponding 2-hydroxy-4:8-dimethylquinoline, and the product worked up as before. In this way from 10 grams of hydroxyquinoline were obtained 3.3 grams of a colourless oil. In order to obtain the pure base it was converted into the picrate, and the base regenerated from the pure salt boiled at $140-141^{\circ}/15$ mm.

The *picrate* was prepared in the manner described for the picrate of 4:8-dimethylquinoline, and was crystallised from dilute alcohol. It forms broad, rectangular, golden-yellow prisms, melting at 224° :

0.1736 gave 0.3374 CO_2 and 0.0566 H_2O . $\text{C}=53.0$; $\text{H}=3.6$.

$\text{C}_{11}\text{H}_{11}\text{N}_3\text{C}_6\text{H}_5\text{O}_7\text{N}_3$ requires $\text{C}=52.8$; $\text{H}=3.6$ per cent.

This salt is very sparingly soluble in cold water, and only moderately so in hot water or alcohol.

4:7-Dimethyl-1:2:3:4-tetrahydroquinoline.

Ten grams of 2-hydroxy-4:7-dimethylquinoline were dissolved in boiling absolute alcohol, and 12 grams of sodium added to the boiling solution in small quantities at a time. The sodium salt of the hydroxyquinoline separates as a spongy mass, but slowly dissolves as the reduction proceeds. The dimethyltetrahydroquinoline was recovered as previously described. Yield, 5 grams.

The base was converted into the picrate, and recovered from the pure picrate by steam distillation from alkaline solution.

4:7-Dimethyl-1:2:3:4-tetrahydroquinoline is a colourless oil, which dissolves in concentrated sulphuric acid with a faint yellow colour, and on addition of a drop of concentrated nitric acid gives a purple-brown coloration. It boils at $136-138^{\circ}/13$ mm., and $268-270^{\circ}/769$ mm.:

0.1456 gave 0.4364 CO_2 and 0.1260 H_2O . $\text{C}=81.8$; $\text{H}=9.3$.

$\text{C}_{11}\text{H}_{15}\text{N}$ requires $\text{C}=82.0$; $\text{H}=9.3$ per cent.

The *picrate* crystallises from dilute alcohol in long, orange-yellow, serrated needles, melting at $155-156^{\circ}$. Its solubilities resemble those of the 4:8-dimethyltetrahydroquinoline picrate already described:

0.1420 gave 0.2728 CO_2 and 0.0598 H_2O . $\text{C}=52.4$; $\text{H}=4.7$.

$\text{C}_{11}\text{H}_{15}\text{N}_3\text{O}_7\text{H}_3\text{O}_2\text{N}_8$ requires $\text{C}=52.3$; $\text{H}=4.6$ per cent.

The *benzoyl* derivative, $\text{C}_{18}\text{H}_{19}\text{ON}$, prepared by the Schotten-Baumann reaction, crystallises from light petroleum in bundles of leaflets, and melts at $84-85^{\circ}$.

Acetoaceto-p-toluidide, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$.

This compound was prepared in the same way as the toluidides already described, and was similar to them in general properties. After crystallisation from ethyl acetate it was obtained in well-formed prisms melting at $94-95^{\circ}$:

0.1356 gave 0.3442 CO_2 and 0.0844 H_2O . $\text{C}=69.2$; $\text{H}=6.9$.

$\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C}=69.1$; $\text{H}=6.8$ per cent.

The corresponding hydroxyquinoline (2-hydroxy-4:6-dimethylquinoline) was obtained by the action of concentrated sulphuric acid, as described before, and was found to agree in melting point and properties with the compound described by Knorr. It was submitted to distillation with zinc dust and reduction by sodium and alcohol, yielding 4:6-dimethyl- and 4:6-dimethyl-1:2:3:4-tetrahydroquinolines respectively.

4:6-Dimethylquinoline.

Ten grams of 2-hydroxy-4:6-dimethylquinoline were distilled with zinc dust. The crude 4:6-dimethylquinoline so obtained was dis-

tilled, yielding 3.5 grams, which were converted into the picrate. The pure base was recovered from the purified picrate, and boiled at $140-141^{\circ}/12$ mm. and $255-256^{\circ}/760$ mm.

4:6-Dimethylquinoline picrate crystallises from dilute alcohol in long, rectangular prisms, melting at $236-237^{\circ}$ (Knorr gives 230°). (Found, C=52.7; H=3.6. Calc., C=52.8; H=3.6 per cent.)

The solubilities are similar to the dimethylquinoline picrates already described.

4:6-Dimethyl-1:2:3:4-tetrahydroquinoline.

Ten grams of 2-hydroxy-4:6-dimethylquinoline were reduced in concentrated boiling alcoholic solution by 24 grams of sodium. The dimethyltetrahydroquinoline was recovered by steam distillation, and after distillation under diminished pressure yielded 4.3 grams of base.

The pure base was obtained from the purified picrolonate by steam distillation in alkaline solution. It boiled at $135-137^{\circ}/15$ mm. and $254-256^{\circ}/750$ mm.

4:6-Dimethyl-1:2:3:4-tetrahydroquinoline is a colourless oil. It dissolves in concentrated sulphuric acid with a deep purple colour, which slowly passes into blue, and finally becomes deep green:

0.1764 gave 0.5296 CO_2 and 0.1482 H_2O . C=81.9; H=9.4.

$\text{C}_{11}\text{H}_{15}\text{N}$ requires C=82.0; H=9.3 per cent.

The picrolonate, prepared in ethereal solution and crystallised from dilute alcohol, crystallises in hard, yellow rhombs, and melts at $204-205^{\circ}$. It is very sparingly soluble in boiling water or alcohol:

0.1494 gave 0.3262 CO_2 and 0.0732 H_2O . C=59.4; H=5.4.

$\text{C}_{11}\text{H}_{15}\text{N}, \text{C}_{10}\text{H}_8\text{O}_5\text{N}_4$ requires C=59.3; H=5.4 per cent.

The picrate is obtained as a gummy solid by precipitating the ethereal solution with light petroleum. It can be recrystallised from benzene, and separates in rectangular plates melting at $116-117^{\circ}$:

0.1162 gave 0.2234 CO_2 and 0.0494 H_2O . C=52.4; H=4.7.

$\text{C}_{11}\text{H}_{15}\text{N}, \text{C}_6\text{H}_5\text{O}_7\text{N}_3$ requires C=52.3; H=4.6 per cent.

The benzoyl derivative, prepared by the Schotten-Baumann reaction, crystallises from dilute alcohol in pearly leaflets melting at $109-110^{\circ}$:

0.1372 gave 0.4094 CO_2 and 0.0880 H_2O . C=81.4; H=7.1.

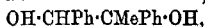
$\text{C}_{18}\text{H}_{19}\text{ON}$ requires C=81.5; H=7.2 per cent.

THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
HERNE HILL, S.E.

XVI.—Optically Active Glycols Derived from the Phenyl-lactic Acids. Part I.

By ALEX. MCKENZIE and GEOFFREY MARTIN.

In a previous paper by McKenzie and Wren (T., 1910, 97, 473) it was shown that *l*-triphenylethylene glycol, $\text{OH}\cdot\text{CHPh}\cdot\text{CPh}_2\cdot\text{OH}$, can be prepared by the action of magnesium phenyl bromide on *l*-benzoin or on methyl *l*-mandelate. The two latter compounds are related in configuration, since *l*-benzoin is prepared from the *l*-mandelamide corresponding with *l*-mandelic acid without the employment of any operation which involves the substitution of a grouping directly attached to the asymmetric atom. The above-mentioned glycol is nevertheless strongly dextrorotatory, the value for the specific rotatory power in acetone solution being $+221.3^\circ$, whereas *l*-benzoin has $[\alpha]_D -118.6^\circ$ in the same solvent. In marked contrast is the rotation of *l*- α -dihydroxy- α -phenylisobutane, $\text{OH}\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{OH}$ (derived from methyl *l*-mandelate), which has $[\alpha]_D -21.6^\circ$ in acetone solution, the levorotation accordingly persisting in this compound. On the other hand, the glycol,



derived from *l*-benzoin, is dextrorotatory, having $[\alpha]_D +34^\circ$.

The present paper contains a description of several glycols which have been prepared from the optically active phenyl-lactic acids, $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ (McKenzie and Humphries, T., 1910, 97, 121; McKenzie and Wren, *ibid.*, 1355), by the application of the Grignard action. The acids possess almost identical rotatory powers in ethyl-alcoholic solution, namely, $[\alpha]_D -18.9^\circ$ and -18.7° respectively for the *l*-acids. In aqueous solution their rotations are also not much different; *d*- α -hydroxy- β -phenylpropionic acid has $[\alpha]_D +22.8^\circ$, and for comparison we have determined the rotation of the *l*- β -hydroxy-acid in aqueous solution, and have found the value $[\alpha]_D -21^\circ$.

The glycols obtained from the *l*- β -hydroxy-acid gave the following values:

	$[\alpha]_D$ in acetone solution.
$\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$	$+3.6^\circ$
$\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$	-57.1
$\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_2\text{Ph})_2\cdot\text{OH}$	-82.8

The depression in rotation caused by the displacement of methyl by phenyl groups is obvious in this series also, and is comparable with the effects observed by Rupe with the menthyl esters of various unsaturated acids. The influence, however, of the introduction of the methylene group between the $\cdot\text{CPh}_2\cdot\text{OH}$ group and the asym-

metric centre is such as to cause the swing round of rotation to be less pronounced than in the case of triphenylethylene glycol.

The glycols derived from the α -hydroxy-acids gave the following values:

	[α] _D in acetone solution.
<i>l</i> -CH ₂ Ph·CH(OH)·CPh ₂ OH	-109.9°
<i>l</i> -CH ₂ Ph·CH(OH)·CMe ₂ OH	-70.8
<i>d</i> -CH ₂ Ph·CH(OH)·CEt ₂ OH	+68.7
<i>d</i> -CH ₂ Ph·CH(OH)·C(CH ₂ Ph) ₂ OH	+7.5

The effect is thus reversed when the methylene group is interposed between the phenyl group and the asymmetric centre.

EXPERIMENTAL.

α -Dihydroxy- $\alpha\alpha$ -triphenylpropanes.

In the preparation of the various Grignard reagents used in the course of the present research it was found to be very convenient to employ an excess of magnesium (from 2 to 4 atoms for each molecule of haloid). Not only is the action completed more quickly than by the usual method, but the formation of hydrocarbons according to the scheme $\text{RMgX} + \text{XR} = \text{R} \cdot \text{R} + \text{MgX}_2$ is also to a certain extent minimised. This modification was suggested by Schmidlin and Massini (*Ber.*, 1909, **42**, 2381).

The optically active β -hydroxy- β -phenylpropionic acids were prepared as described by McKenzie and Humphries (*T.*, 1910, **97**, 121). An ethereal solution of the *d*-acid (3 grams) was gradually added to the Grignard reagent prepared from bromobenzene (38 grams) and magnesium (24 grams), and the mixture then heated for fifteen minutes. After decomposition in the usual manner with ice and sulphuric acid, the diphenyl was removed from the product by means of light petroleum, and the crude glycol (2.6 grams) was purified by crystallisation from ethyl alcohol. Yield, 1.7 grams.

d- α -Dihydroxy- $\alpha\alpha$ -triphenylpropane, $\text{OH} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CPh}_2 \cdot \text{OH}$, separates from ethyl alcohol in colourless, rectangular crystals, and melts at 147–148°. It is very sparingly soluble in water. It dissolves readily in boiling light petroleum (b. p. 60–80°) or benzene, separating on cooling. It is readily soluble in acetone or ether. When added to concentrated sulphuric acid, it becomes scarlet, the solution being reddish-orange, and exhibiting slight fluorescence. For analysis it was dried at 100°:

0.1496 gave 0.4535 CO₂ and 0.0885 H₂O. C=82.7; H=6.6.

C₂₁H₂₀O₂ requires C=82.9; H=6.6 per cent.

The specific rotation was determined. In acetone solution:

$l=4$, $c=1.1368$, $\alpha_D^{20} = -0.14^\circ$, $[\alpha]_D^{20} = -3.1^\circ$.

In benzene solution:

$$l=4, c=1.174, \alpha_D^{18} + 0.16^\circ, [\alpha]_D^{18} + 3.4^\circ.$$

l- α -Dihydroxy- $\alpha\alpha$ -triphenylpropane, prepared from *l*- β -hydroxy- β -phenylpropionic acid, is similar in properties to its *d*-isomeride:

0.1156 gave 0.3498 CO₂ and 0.0681 H₂O. C=82.5; H=6.6.

C₂₁H₂₀O₂ requires C=82.9; H=6.6 per cent.

In acetone solution:

$$l=4, c=2.0828, \alpha_D^{18} + 0.30^\circ, [\alpha]_D^{18} + 3.6^\circ.$$

In benzene solution:

$$l=4, c=1.1632, \alpha_D^{18} - 0.17^\circ, [\alpha]_D^{18} - 3.7^\circ.$$

r- α -Dihydroxy- $\alpha\alpha$ -triphenylpropane, prepared from *r*- β -hydroxy- β -phenylpropionic acid, separates from benzene in colourless, rectangular crystals, and melts at 127–128°:

0.1837 gave 0.5564 CO₂ and 0.112 H₂O. C=82.6; H=6.8.

C₂₁H₂₀O₂ requires C=82.9; H=6.6 per cent.

This glycol may also be prepared conveniently by the interaction of magnesium phenyl bromide and methyl *dl*- β -hydroxy- β -phenylpropionate, OH·CHPh·CH₂·CO₂Me, a viscid oil, which boils at 158–161°/17–18 mm.:

0.2095 gave 0.509 CO₂ and 0.1285 H₂O. C=66.3; H=6.9.

C₁₀H₁₂O₃ requires C=66.6; H=6.7 per cent.

The three glycols described exhibit a strong green triboluminescence.* In quoting several cases where *d*- and *l*-modifications exhibited triboluminescence whereas the *r*-isomeride did not, Tschugaev (*Ber.*, 1901, **34**, 1820) suggests that there is possibly some connexion between this phenomenon and optical activity; such a connexion appears, however, to be unlikely.

$\alpha\gamma$ -Dihydroxy- α -phenylisopentanes.

Attempts to obtain the *l*-glycol by the action of magnesium, methyl iodide on the *l*-hydroxy-acid having failed, the active esters were prepared by the hydrogen chloride method from the active acids and methyl alcohol. Repeated distillation under diminished pressure should, however, be avoided, since partial racemisation apparently takes place somewhat readily under the influence of heat. The maximum rotation observed for the *d*-ester was $[\alpha]_D + 17.4^\circ$ for $c=4.558$ in ethyl-alcoholic solution, and for the *l*-ester $[\alpha]_D - 17.0^\circ$ under similar conditions. Those values are probably correct for the optically pure esters, the *d*-acid (free from the *r*-isomeride) having been prepared from the *d*-ester with

* The parent hydroxy-acids are also triboluminescent, although to a less degree than the glycols.

$\alpha_D^{20} + 17.4^\circ$ by saponifying it at the ordinary temperature with aqueous alcoholic potassium hydroxide.

Six grams of methyl *d*- β -hydroxy- β -phenylpropionate were added gradually within ten minutes to an excess of magnesium methyl iodide prepared from 37 grams of methyl iodide, and the product was allowed to remain overnight before decomposition with ice and ammonium chloride. The crude material was purified by crystallisation from a mixture of benzene and light petroleum, when 1.7 grams of the glycol were obtained.

d- $\alpha\gamma$ -Dihydroxy- α -phenylisopentane, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$, separates in colourless, silky, rectangular crystals, and melts at $70-71^\circ$. It is practically insoluble in water, sparingly soluble in light petroleum, and easily so in cold benzene, acetone, or ether. Its behaviour towards sulphuric acid is similar to that exhibited by the $\alpha\gamma$ -dihydroxy- $\alpha\alpha$ -triphenylpropanes:

0.1368 gave 0.368 CO_2 and 0.1138 H_2O . $\text{C} = 73.4$; $\text{H} = 9.3$.

$\text{C}_{11}\text{H}_{16}\text{O}_2$ requires $\text{C} = 73.3$; $\text{H} = 9.0$ per cent.

Its rotation was determined in acetone solution:

$l = 2$, $c = 4.502$, $\alpha_D^{15} + 5.11^\circ$, $[\alpha]_D^{15} + 56.8^\circ$.

In benzene solution:

$l = 2$, $c = 3.742$, $\alpha_D^{15} + 5.41^\circ$, $[\alpha]_D^{15} + 72.3^\circ$

l- $\alpha\gamma$ -Dihydroxy- α -phenylisopentane, prepared from methyl *l*- β -hydroxy- β -phenylpropionate, melts at $70-71^\circ$:

0.148 gave 0.3975 CO_2 and 0.1192 H_2O . $\text{C} = 73.2$; $\text{H} = 9.0$.

$\text{C}_{11}\text{H}_{16}\text{O}_2$ requires $\text{C} = 73.3$; $\text{H} = 9.0$ per cent.

In acetone solution:

$l = 2$, $c = 4.746$, $\alpha_D^{15} - 5.42^\circ$, $[\alpha]_D^{15} - 57.1^\circ$.

In benzene solution:

$l = 2$, $c = 3.676$, $\alpha_D^{15} - 5.32^\circ$, $[\alpha]_D^{15} - 72.3^\circ$.

r- $\alpha\gamma$ -Dihydroxy- α -phenylisopentane, prepared from methyl *d*- β -hydroxy- β -phenylpropionate, separates from light petroleum (b. p. $60-80^\circ$) in colourless, rectangular crystals. It may also be crystallised from ethyl alcohol:

0.216 gave 0.5806 CO_2 and 0.17 H_2O . $\text{C} = 73.3$; $\text{H} = 8.8$.

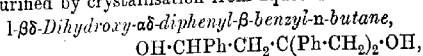
$\text{C}_{11}\text{H}_{16}\text{O}_2$ requires $\text{C} = 73.3$; $\text{H} = 9.0$ per cent.

No triboluminescence was observed with the isomeric $\alpha\gamma$ -dihydroxy- γ -phenyl- $\alpha\alpha$ -dimethylpropanes.

l- $\beta\delta$ -Dihydroxy- $\alpha\delta$ -diphenyl- β -benzyl-*n*-butane.

An ethereal solution of 3 grams of methyl *l*- β -hydroxy- β -phenylpropionate was gradually added to the Grignard reagent prepared from 28 grams of benzyl chloride, and the mixture boiled for one

hour. After decomposition of the additive product, the ether was distilled off, and the dibenzyl then removed by steam distillation. The residual resin was finally caused to solidify by covering it with *N*/10-aqueous potassium hydroxide containing a little ethyl alcohol, and allowing it to remain thus for three days. The glycol was purified by crystallisation from aqueous alcohol. Yield, 4.6 grams.



separates from aqueous ethyl alcohol in colourless needles, and melts at 85–86°. It may also be crystallised from light petroleum, in which it is sparingly soluble at the ordinary temperature. It is very soluble in cold chloroform, benzene, or ethyl alcohol. It dissolves sparingly in cold concentrated sulphuric acid, the solution being yellow:

0.1344 gave 0.41 CO₂ and 0.0888 H₂O. C = 83.2; H = 7.4.
C₂₃H₂₄O₂ requires C = 83.1; H = 7.3 per cent.

In acetone solution:

$$l=2, c=3.655, \alpha_D^{18} - 6.05^\circ, [\alpha]_D^{18} - 82.8^\circ.$$

In benzene solution:

$$l=2, c=3.761, \alpha_D^{18} - 6.58^\circ, [\alpha]_D^{18} - 87.5^\circ.$$

In ethyl-alcoholic solution:

$$l=2, c=4.463, \alpha_D^{16} - 6.67^\circ, [\alpha]_D^{16} - 74.7^\circ.$$

This glycol exhibited a feeble triboluminescence.

Attempts to prepare the ethyl, *o*-tolyl, and naphthyl glycols were unsuccessful, probably owing to the dehydrating effect of the Grignard reagents.

1-αβ-Dihydroxy-ααγ-triphenylpropane.

α-α-Hydroxy-*β*-phenylpropionic acid was resolved into its optically active components according to the method of McKenzie and Wren (T., 1910, **97**, 1355).*

An ethereal solution of *l-α*-hydroxy-*β*-phenylpropionic acid (3 grams) was added to the Grignard reagent prepared from 38 grams of bromobenzene. The mixture was boiled for three hours. The crude glycol, obtained after removal of the diphenyl by distillation in steam, amounted to 4.1 grams, and was crystallised first from a mixture of benzene and light petroleum and then three times from light petroleum (b. p. 60–80°). Yield, 2.3 grams.

* Ehrlich and Jacobsen (*Ber.*, 1911, **44**, 888) have made the interesting observation that *d-α*-hydroxy-*β*-phenylpropionic acid is produced by the growth of *Gibbula lactis* on *r*-phenylalanine, the properties of the *d*-hydroxy-acid being in accordance with those described by McKenzie and Wren (*loc. cit.*).

1- α -Dihydroxy- α -triphenylpropane, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{CPh}_2\cdot\text{OH}$, separates in colourless, rectangular crystals, and melts at $96-97^\circ$. It is sparingly soluble in cold light petroleum, and easily so in benzene. When added to cold concentrated sulphuric acid, it becomes scarlet, and the solution is yellow to orange in tint:

0.1228 gave 0.3736 CO_2 and 0.0734 H_2O . $\text{C}=83.0$; $\text{H}=6.7$.

$\text{C}_{21}\text{H}_{20}\text{O}_2$ requires $\text{C}=82.9$; $\text{H}=6.6$ per cent.

In acetone solution:

$l=2$, $c=2.502$, $\alpha_D^{25} -5.50^\circ$, $[\alpha]_D^{25} -109.9^\circ$.

In benzene solution:

$l=2$, $c=2.753$, $\alpha_D^{16} -7.60^\circ$, $[\alpha]_D^{16} -138.0^\circ$.

This glycol exhibited a vivid triboluminescence.

1- β -Dihydroxy- α -phenylisopentane.

Methyl 1- α -hydroxy- β -phenylpropionate, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{Me}$, prepared by the esterification of the *l*-hydroxy-acid with methyl alcohol and hydrogen chloride, boils at $155^\circ/17$ mm. It became solid on the addition of a nucleus of the ethyl *l*-ester (McKenzie and Barrow, T., 1911, **99**, 1922), and then melted at $47.5-48.5^\circ$. It separates from ethyl alcohol in needles, and may also be crystallised conveniently from light petroleum. It is readily soluble in acetone or benzene. Its behaviour resembles that of the ethyl ester, inasmuch as it is dextrorotatory in ethyl-alcoholic solution:

$l=2$, $c=3.131$, $\alpha_D^{18.5} +0.40^\circ$, $[\alpha]_D^{18.5} +6.4^\circ$.

In acetone solution:

$l=2$, $c=3.879$, $\alpha_D^{19.5} -0.66^\circ$, $[\alpha]_D^{19.5} -8.5^\circ$.

In benzene solution:

$l=2$, $c=3.092$, $\alpha_D^{19} -0.75^\circ$, $[\alpha]_D^{19} -12.1^\circ$.

0.1353 gave 0.33 CO_2 and 0.0815 H_2O . $\text{C}=66.5$; $\text{H}=6.7$.

$\text{C}_{16}\text{H}_{18}\text{O}_3$ requires $\text{C}=66.6$; $\text{H}=6.7$ per cent.

The methyl *l*-ester (3.4 grams) was added to the Grignard reagent prepared from methyl iodide (30 grams). The yield of pure glycol amounted to 2.5 grams.

1- β -Dihydroxy- α -phenylisopentane, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{OH}$, crystallises in colourless prisms, and melts at $73-74^\circ$. It is easily soluble in ether, ethyl alcohol, acetone, or benzene, and may be crystallised conveniently from light petroleum (b. p. $60-80^\circ$), in which it is sparingly soluble at the ordinary temperature. Its solution in cold concentrated sulphuric acid is yellowish-brown, and it exhibits a pronounced green fluorescence:

0.134 gave 0.3605 CO₂ and 0.1083 H₂O. C=73.4; H=9.0.

C₁₁H₁₆O₂ requires C=73.3; H=9.0 per cent.

In acetone solution:

$l=2$, $c=3.424$, $\alpha_D^{20} - 4.85^\circ$, $[\alpha]_D^{20} - 70.8^\circ$.

In benzene solution:

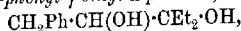
$l=2$, $c=2.898$, $\alpha_D^{20} - 3.92^\circ$, $[\alpha]_D^{20} - 67.6^\circ$.

The triboluminescence exhibited by this glycol was very faint.

d-βγ-Dihydroxy-α-phenyl-γ-ethyl-n-pentane.

This glycol was prepared by the interaction of ethyl *d-α*-hydroxy-β-phenylpropionate (3 grams) and the Grignard reagent obtained from ethyl iodide (25 grams). The crude solid (2.7 grams) was purified by three crystallisations from light petroleum.

d-βγ-Dihydroxy-α-phenyl-γ-ethyl-n-pentane,



separates in rectangular needles, and melts at 74—75°. It is readily soluble in cold ethyl alcohol, ether, benzene, or acetone, and sparingly so in cold light petroleum. Its solution in cold concentrated sulphuric acid is yellow and fluorescent:

0.1177 gave 0.3234 CO₂ and 0.101 H₂O. C=74.9; H=9.6.

C₁₃H₂₀O₂ requires C=74.9; H=9.7 per cent.

In acetone solution:

$l=2$, $c=2.54$, $\alpha_D^{18} + 2.98^\circ$, $[\alpha]_D^{18} + 58.7^\circ$.

In benzene solution:

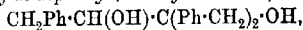
$l=2$, $c=2.734$, $\alpha_D^{18} + 2.49^\circ$, $[\alpha]_D^{18} + 45.5^\circ$.

The compound was strongly triboluminescent.

d-βγ-Dihydroxy-αδ-diphenyl-β-benzyl-n-butane.

The additive compound formed from the interaction of ethyl *d-α*-hydroxy-β-phenylpropionate (2.1 grams) and the Grignard reagent prepared from 23 grams of benzyl chloride was decomposed by ice and sulphuric acid. The glycol is sparingly soluble in ether, and it accordingly separated. It was purified by crystallisation from ethyl alcohol. Yield, 1.8 grams.

d-βγ-Dihydroxy-αδ-diphenyl-β-benzyl-n-butane,



is sparingly soluble in cold and hot ethyl alcohol, from which it separates in colourless needles, m. p. 182.5—183.5°. It is sparingly soluble in cold ether, benzene, or light petroleum, and moderately so in cold acetone. It is not so soluble in cold sulphuric acid as the other glycols; its solution is orange-coloured:

0.1016 gave 0.3094 CO₂ and 0.0665 H₂O. C=83.1; H=7.3.

C₂₀H₂₄O₂ requires C=83.1; H=7.3 per cent.

In acetone solution:

$$l=4, c=0.5016, \alpha_D^{18} + 0.15^\circ, [\alpha]^{18} + 7.5^\circ.$$

In benzene solution:

$$l=4, c=0.3928, \alpha_D^{18} - 0.35^\circ, [\alpha]^{18} - 22.3^\circ.$$

The compound exhibited a feeble triboluminescence.

The expenses of this investigation have been mainly met by a grant from the Government Grant Committee of the Royal Society, for which we are glad to take this opportunity of expressing our thanks.

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XVII.—*Dibenzyl- and Diphenyl-silicols and -silicones.*

By GEOFFREY MARTIN.

KIPPING (T., 1912, 101, 2108) states that I (*Ber.*, 1912, 45, 403) "gave a very erroneous account" of diphenylsilicol, suggests that I was "misled" by false analogies (p. 2112), that "the difficulties presented by the investigation . . . were altogether exceptional, and might have led into error a much more experienced chemist" (p. 2112), and says that he "failed to confirm" my "more important experiments" (p. 2108). The reader, without my paper before him, and with no special knowledge of the subject, would certainly gather that Kipping had arrived at conclusions very different from mine, and that I had made a series of grave mistakes, which he now put right. That such conclusions would be entirely incorrect is shown by a brief contrast between Kipping's and my results:

Properties of Diphenylsilicol.

KIPPING (T., 1912, 101,
2106—2166).

1. Two "crystalline modifications" (p. 2112).
2. Both forms decompose on heating, evolving water with effervescence (pp. 2112, 2122, 2123, 2136, etc.).
3. Both forms liquefy at the moment of decomposition, forming silicones (pp. 2109, 2136).
4. The form with the higher liquefying point is the more stable (pp. 2112, 2124).

MARTIN (*Ber.*, 1912, 45,
403—409).

1. Two "*Modifikationen*" composed of different crystals (pp. 405—406).
2. Both forms decompose on heating, evolving water with effervescence (p. 405).
3. Both forms liquefy at the moment of decomposition, forming a glue-like product (p. 406).
4. The form with the higher liquefying point appears to be the more stable (p. 406).

*Properties of Diphenylsilicol (continued).*KIPPING (T., 1912, 101,
2106—2166).

5. The lower liquefying form can pass into the higher form, either spontaneously (pp. 2120, 2124) or on heating (pp. 2112, 2124).
6. The temperature of liquefaction or decomposition varies with rate of heating and state of division of the substance (p. 2122).
7. The one form liquefies with decomposition below 132°,* the other at about 160° (pp. 2112, 2124).
8. Both forms:
soluble in potassium hydroxide solution;
readily soluble in ether;
sparingly soluble in chloroform;
practically insoluble in light petroleum (p. 2122).
9. Pure specimens "usually decompose and liquefy completely below 132°,* although very occasionally the decomposition does not occur until the temperature has been raised to about 160°" (p. 2112).

MARTIN (Ber., 1912, 45,
403—409).

5. The one form appears capable of passing into the other, and vice versa (p. 406).
6. The temperature of liquefaction (decomposition) varies with the rate of heating (p. 405).
7. The one form liquefies with decomposition at about 140°,* the other at about 160° (p. 405).
8. Both forms:
soluble in potassium hydroxide solution;
readily soluble in ether;
sparingly soluble in chloroform;
only sparingly soluble in light petroleum (p. 405).
9. Die so erhaltene Krystallmasse schmolz bei ungefähr 160° unter Aufschäumen (infolge Abspaltung von Wasser); der Schmelzpunkt schwankte etwas mit der Schnelligkeit des Erhitzens, und in einigen Fällen wurden auch Produkte gewonnen, die sich bereits bei 140° verflüssigten (p. 405).

* The difference of about 8° between the decomposition points of my modification and that of Kipping is probably due to the fact that I heated more rapidly, using a larger quantity of material than he did.

Since Kipping's account of diphenylsilicol agrees closely with mine, his remark (*loc. cit.*, p. 2108, footnote) that in my paper I "unfortunately . . . gave a very erroneous account" of diphenylsilicol, is unjustifiable, and all the more so as he has added nothing of importance to the facts already published in my paper (*loc. cit.*).

Turning to Kipping's statement (*loc. cit.*, p. 2108) that he "failed to confirm" some of my "more important experiments," the following tabulation of my results and those obtained by Kipping shows that the "confirmation" is close (compounds marked † are described for the first time):

KIPPING (*loc. cit.*).

1. "Dianhydrotetraphenylsilicomediol," massive, transparent, rhomboidal crystals, m. p. 111—112° (p. 2131).

MARTIN (*loc. cit.*).

1. † "Grosse, durchsichtige, flache Rhomben," "die so erhaltenen Krystalle schmolzen bei 110° bezw. nach nochmaligem umföhen bei 111°" (p. 407).

* Kipping misquotes (p. 2129) my melting point as 100—111°.

KIPPING (*loc. cit.*).

2. † "Anhydrosidiphenylsilicanediol," m. p. 113–114°.
3. Silicone, $(\text{SiPh}_2\text{O})_n$, m. p. 188–189° (Dilthey's silicone).
4. † Silicone, $(\text{SiPh}_2\text{O})_n$, m. p. 200–201°, "crystals, melting fairly sharply at 184–186°" were obtained; "this apparently pure . . . compound . . . by repeated fractional crystallisation . . . was gradually resolved into the pure compound, melting at 200–201° . . ." (p. 2140).
5. Existence not disputed (p. 2126).
6. " " "
7. *Phenylbenzylsilicol*,
 $\text{SiPh}(\text{CH}_2\text{Ph})(\text{OH})_2$,
 silky needles, soluble in potassium hydroxide, m. p. 106°, when rapidly heated. Resembles dibenzylsilicol, decomposed in solution by hydrochloric acid (p. 2164).

MARTIN (*loc. cit.*).

2. Not isolated in a pure state.
3. Silicone, $(\text{SiPh}_2\text{O})_n$, m. p. 188° (Dilthey's silicone).
4. "In sehr kleinen Quantitäten erhielt ich hierbei auch zwei krystallinische Körper vom Schmp. 125° bzw. 186°, die mit dem Diltheyschen Silicon nicht identisch und wahrscheinlich bisher noch nicht beschrieben sind. Ich habe sie jedoch nicht in genügenden Mengen gewinnen können, um ihre Natur festzustellen" (p. 408).
5. † Silicone, $(\text{SiPh}_2\text{O})_n$, m. p. over 360°, white, amorphous powder.
6. † Silicone, $(\text{Si}(\text{CH}_2\text{Ph})_2\text{O})_n$, m. p. about 200°, white, amorphous powder.
7. † *Phenylbenzylsilicol*,
 $\text{SiPh}(\text{CH}_2\text{Ph})(\text{OH})_2$,
 white, crystalline substance, m. p. 104°. Resembles dibenzylsilicol, m. p. 101°. When moist, is decomposed by hydrochloric acid fumes (p. 405).

I now deal with a misrepresentation of my paper. Kipping requested me to look for two "isomerides" of diphenylsilicol, Kipping and Robison (T., 1908, **93**, 441) having just described two "isomerides" of dibenzylsilicol, one melting at 74° and the other at 101°, which were "unaccountable" on the current ideas of stereoisomerism. This was the origin of my paper. However, Kipping and Robison's new "isomerides" were really substances very different from each other in molecular structure and molecular weight; the one "isomeride," m. p. 74°, having the complex structure $\text{HO}\cdot\text{Si}(\text{C}_7\text{H}_7)_2\cdot\text{O}\cdot\text{Si}(\text{C}_7\text{H}_7)_2\cdot\text{OH}$, and crystallising with one molecule of water, whilst the other "isomeride," m. p. 101°, is the "real" dibenzylsilicol (T., 1912, **101**, 2143). Kipping, however, now asserts that I have erroneously described two "isomeric" forms of diphenylsilicol; thus he says (P., 1912, **28**, 244):

"The *isomeric* 'diphenylsilicols' described by Martin (*Ber.*, 1912, **45**, 403) as melting at about 140° and 160° respectively, were probably impure specimens of diphenylsilicanediol (diphenylsilicol), and the methods which he gave for the conversion of these supposed isomerides into one another do not bring about any isomeric change."

In the *Transactions* (*loc. cit.*) he amplifies his statements, referring to my "isomerides" on p. 2108 and p. 2110, whilst on p. 2112 he says:

"there does not seem to be any evidence of the existence of

the isomeric diphenylsilicanediols (diphenylsilicols) described by Martin, and judging from the methods of preparation and the decomposing points of his supposed isomerides, both must be regarded as impure specimens of the diol (diphenylsilicol). In justice to Martin, however, it should perhaps be pointed out that not only was he misled by a presumed analogy between dibenzylsilicanediol and diphenylsilicanediol, etc."

On p. 2125 he even "explains" how my error arose:

"One further point remains to be considered, namely, how Martin was led to believe that the preparations which he regarded as isomeric diphenylsilicols could be transformed one into the other by the methods which he describes (*loc. cit.*). According to his statements, when the "isomeride" decomposing at about 160° was dissolved in an aqueous solution of potassium hydroxide, and the solution then treated with acids, the "isomeride" decomposing at about 144° was obtained, but if alcoholic potassium hydroxide was used, the original "isomeride" decomposing at about 160° was precipitated. These statements are doubtless incorrect in so far as any question of isomerism is concerned, but . . . the actual observations are to be accounted for as follows, etc."

Now all this is most misleading and inaccurate, because in the whole of my paper in the *Berichte* (*loc. cit.*) not a single mention or reference, direct or indirect, is made of the existence of isomeric diphenylsilicols! Indeed, I actually use the same words as Kipping ("modifications"), and give no speculations of any kind in my paper regarding the molecular structure of my two "modifications"; even the abstract of my paper (A., 1912, 102, i, 404) refers to two "forms" only.

Kipping also denies (see preceding quotations) that I transformed one modification of diphenylsilicol into the other, and vice versa. Yet he himself quotes several cases of the change of one modification into the other (see *loc. cit.*, pp. 2112, 2120, 2123, 2124), and on p. 2124 states that this is a result which "appears to be fully established," so that it is not apparent why he should doubt my own statements to the same effect. Moreover, his "explanation" (p. 2125) of my "transformations," based on the assumption of the presence of much impurity insoluble in potassium hydroxide, is incorrect for the simple reason that I isolated my two modifications in a pure form, both soluble in potassium hydroxide without giving a residue. In the first place, starting from my product of low melting point, I obtained by careful and laborious crystallisation (which extended over many weeks) a pure specimen of the modification of lower melting point (m. p. 140°), the analysis of which agreed well with the formula $\text{SiPh}_2(\text{OH})_2$, and the compound was completely soluble

in potassium hydroxide to a perfectly clear solution. Now this substance was simply Kipping's diphenylsilicol of lower melting point (likewise obtained by a process of crystallisation from impure residues! see p. 2120), the difference between the decomposing points (m. p.'s) given by him and myself being simply due to the different rates of heating different quantities of material. In the second case my modification of higher decomposing point (160°) was also obtained pure by week-long continuous recrystallisation of the product of high melting point. Estimations of carbon, hydrogen, and silicon agreed correctly with the formula $\text{SiPh}_2(\text{OH})_2$, and the compound dissolved in potassium hydroxide without any residue. Consequently, as both modifications gave correct analyses, were different in crystalline appearance even to the naked eye, differed by at least 20° in their liquefying points, differed also in their solubilities, and were both completely soluble without residue in aqueous potassium hydroxide, I must, until the contrary is distinctly proved, reaffirm that my two modifications of diphenylsilicol do most undoubtedly exist, and that Kipping has merely "rediscovered" them in his newly-described two "crystalline modifications" of diphenylsilicol.

Lastly, I wish to point out that Kipping's "explanation" (p. 2125) of my results is really no explanation at all. The cause of the rise of liquefying point of the diphenylsilicol from 140° (Kipping, 132°) to 160° is, according to Kipping's own view (*loc. cit.*, pp. 2112, 2124), simply due to the change from one crystalline modification (liquefying at 132° or 140°) into another crystalline state (liquefying at 160°). Kipping does not consider that a trace of "impurity" of itself would cause the liquefying points to rise* by at least 20°, but merely acts, in his own words (p. 2124), in "causing the crystalline transformation of the diol to take place." Hence, even if my impure substance did contain a small trace of "impurity," it would, so long as it melted at 160°, according to Kipping's own explanation, still be in the one crystalline state, whilst when its melting point fell to 140° (132° Kipping) this would likewise be solely due to it passing into the other crystalline state. So that, on Kipping's own "explanation," I must have had the two crystalline modifications in my hands!

Kipping finally concludes (p. 2123):

"It seems necessary to conclude that diphenylsilicanediol (diphenylsilicol) is dimorphous; that the crystalline form which . . . decomposes below 132° may pass into a more stable one, which does not decompose until about 160°."

There seems little difference between this and my earlier conclu-

* A trace of impurity* would rather tend to depress the liquefying point.

sion (*loc. cit.*) that two modifications of diphenylsilicol exist, one with the liquefying point 160° , described as "gegenüber hohen Temperaturen etwas widerstandfähiger war, als die andere" (Martin, *loc. cit.*, p. 406), and the other with a lower liquefying point of about 140° (the exact temperature depending on rate of heating and amount of material heated), and that one form could pass into the other, and vice versa.

XVIII.—*The Photography of Absorption Spectra.*

By THOMAS RALPH MERTON, B.Sc.(Oxon.).

ALMOST all the work on absorption spectra in recent years has been carried out by Hartley and Huntington's method, which consists in photographing a series of spectra of a light source on the same plate through increasing thicknesses of the absorbing substance. By measuring the wave-lengths at which "absorption begins" with the varying thicknesses of solution, a curve may be drawn which represents to some extent the nature of the absorption. The results obtained by this method are only of a very qualitative nature, and Houstoun and his colleagues in a series of papers (*Proc. Roy. Soc. Edin.*, 1911, **31**, 521) have obtained accurate curves of the extinction-coefficients of a number of solutions by the use of a spectrophotometer. A similar method has been used by the author in an investigation of the absorption of uranous chloride solutions (*Proc. Roy. Soc.*, 1912, **A**, **87**, 138).

Whilst measurements with the spectrophotometer can be made to give accurate quantitative results, it must be admitted that a considerable amount of practice is required before concordant readings can be obtained, and the probable error of the observations varies with the wave-length of the light used. It seems, therefore, desirable to find some means of obtaining quantitative results by a simple photographic method.

The objections to the older photographic method may be summarised as follows:

- (i) The point where "absorption begins," which is used in plotting the curves, is always somewhat indefinite.
- (ii) The sensitiveness of the photographic plate varies with light of different wave-length. This not only introduces errors in the shape of the curve, but may in certain circumstances give a wrong reading of the maximum.
- (iii) There is no linear relationship between the density of the

image on the photographic plate and the intensity of the light which produces it.

(iv) The density of the image is not proportional to the product of the intensity of the light by the time of exposure, that is to say, doubling the time of exposure and halving the intensity of the light will not produce the same effect on the photographic plate.

It is evident, therefore, that on account of the anomalous behaviour of the photographic plate, any method which is to give accurate results must be a null method. It must comply with the principle laid down by Houstoun (*loc. cit.*), that two sources of light can only be considered of equal intensity when, in the same time, they produce images of equal density on adjacent portions of the same photographic plate.

A number of experiments were made by the following method, which is similar in principle to that used by Houstoun in his investigations in the ultra-violet.

The light from a straight filament Nernst lamp, after passing through a rectangular glass tank to remove heat rays, was made approximately parallel by a collimating lens. It then passed through two nicol prisms and a glass cell to the slit of the spectrograph. The rotation of one of the nicols could be read on a divided circle. It was thus possible to set the nicols to any desired extinction. The spectrograph used was a large Hilger wave-length spectroscope with a 21-inch focus spectrograph attachment in place of the telescope. It was provided with a wave-length scale, which could be photographed on the plate adjacent to the spectra. The method consists in taking a number of spectra on the same plate in the following manner. Suppose the thirteen exposures were made on the plate. The cell was filled with the solution to be examined, and the angle between the nicols was set to zero. With this arrangement strips 1, 4, 7, 10, and 13 were exposed, the time of exposure being accurately controlled by a stop-watch and a photographic shutter. The cell was now replaced by an exactly similar cell filled with the solvent, and strips 2, 3, 5, 6, 8, 9, 11, and 12 were exposed through a series of different densities which were obtained by rotating one of the nicols. We thus have on the plate five absorption spectra, with a photograph taken through a known density adjacent to each. It is therefore only necessary to pick out the wave-lengths on each strip at which the density is the same as that of the adjacent standard strip.

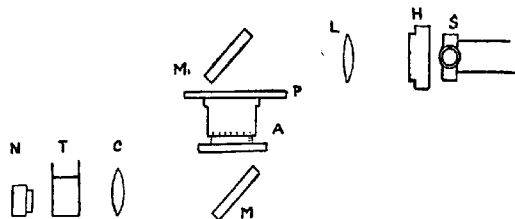
This gives the necessary data for plotting a quantitative extinction curve.

There is, however, an objection to this method, namely, that there is one particular density of the photographic plate at which

the points of equal density on adjacent strips can be accurately found. This is due partly to the form of the curve connecting the intensity of the light with the density which it produces on the plate, but chiefly to the fact that the points of equal density in either very faint or very dense regions are hard to detect. This might be overcome by varying the exposure on the different sets of strips (taking care that each strip has had the same exposure as those with which it is to be compared). Practically, however, this involves very short exposures, which are liable to be inaccurate, for low extinctions, and very long exposures, which makes the method laborious, at high extinctions. A method has been devised, which, it is believed, overcomes these difficulties and provides a simple and accurate method of obtaining extinction curves.

After examining a number of the so-called neutral-tinted glass plates, it was found that the neutral screens supplied by Messrs.

FIG. 1.



Sanger-Shepherd (which are made of an emulsion between two glass plates) have an extinction-coefficient which is practically constant throughout the visible spectrum. This was verified by means of a Houston spectrophotometer.

The method finally adopted was to photograph a series of strips through a neutral plate of carefully standardised extinction, and to photograph between these the spectrum through different thicknesses of the absorbing substance. By choosing a suitable time of exposure the points of equal extinction can be made to occur in each pair of strips at the density best suited for comparison.

A diagram of the apparatus used is shown in Fig. 1. The light from the Nernst lamp *N*, after passing through the water tank *T* and the collimating lens *C*, is twice reflected by the mirrors *MM*, and is concentrated on the slit *S* by the lens *L* after passing through the photographic shutter *H*. A Zeiss variable absorption cell *A* was placed between the mirrors *MM*. The thickness of the absorbing layer in this cell can be accurately measured by means of a screw

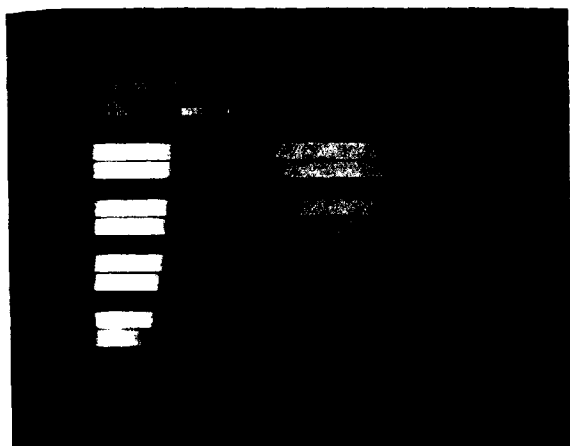
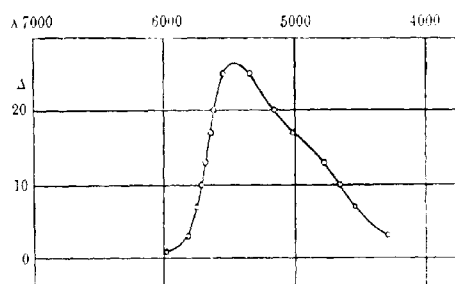


FIG. 2.



[*Te. 1900*, p. 126.

adjustment, and the instrument has been found to be admirably suited to the work.

In conducting the experiment, the cell *A* was filled with the pure solvent, and the standardised plate *P* was laid on it. ($\Delta=1$ has been found to be a suitable density for the standard plate.) Strips 1, 4, 7, 10, and 13 were exposed. The plate was removed, and the cell filled with the solution to be investigated. Strips 2, 3, 5, 6, 8, 9, 11, and 12 were now exposed through various thicknesses of solution. As a typical example is given the plate taken of an aqueous solution of magenta, together with the extinction curve (Fig. 2) drawn from it.

In conclusion, it may be said that the method offers very little practical difficulty; the time taken in the measurement is little longer than with the method of Hartley, and quantitative results can be obtained without involving the use of costly apparatus.

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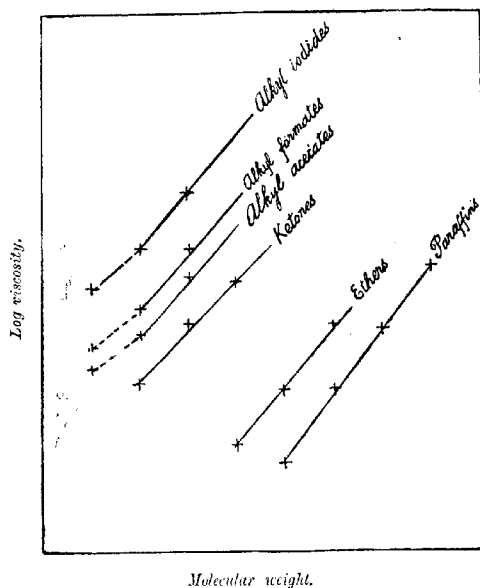
XIX.—*The Relation between Viscosity and Chemical Constitution. Part VI. Viscosity an Additive Function.*

By ALBERT ERNEST DUNSTAN AND FERDINAND BERNARD THOLE.

SOME time ago (*J. Chim. Phys.*, 1909, 7, 210) we drew attention to the fact that a linear relationship exists between molecular weights and logarithms of viscosity in several homologous series. Having in the meantime amassed more experimental material, we desire in the present communication further to develop this generalisation. Owing to the kindness of Dr. Pickard, we have had the opportunity of examining two of the long homologous series prepared by himself and Mr. Kenyon (*T.*, 1911, 99, 45). In one of these series, the methylalkylcarbinols, all the eight members examined, ranging from isopropyl alcohol to methylnonylcarbinol, give log viscosities which lie on a straight line. In the other series, the isopropylalkylcarbinols, the agreement is scarcely so good, but a glance at the figure will show that a straight line adequately represents the relationship between molecular weight and log viscosity. Further, in collaboration with Dr. Hilditch (see Part VII. of this series), we have examined a long series of dibasic esters from the oxalic to the sebacic term. Little regularity is met with in this case until the

first three members are passed, since conjugation effects are pronounced in these cases, but from glutaric ester onwards the linearity of the curve becomes marked. Gartenmeister (*Zeitsch. physikal. Chem.*, 1890, **6**, 524) measured the viscosities of the first nine members of the fatty acids at 20°, and we find that on plotting log viscosity against molecular weights a linear curve is afforded from the third member onwards. Adding to these cases, all of which embody an homologous series of some length, the measurements of Thorpe and Rodger (*Phil. Trans.*, 1894, *A.*, **185**, 397)

FIG. 1.

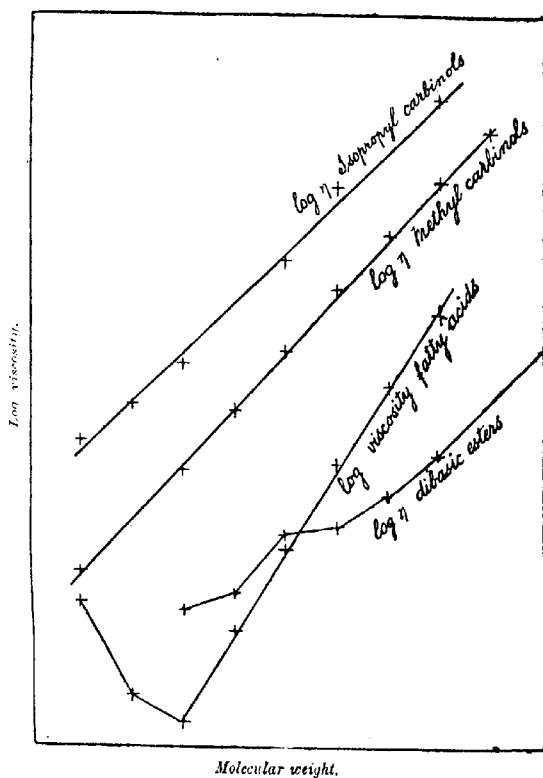


for the first four or five members of some ten homologous series, we find the same linear relationship, and we suggest that additive values of log viscosity for the more important radicles may well be deduced.

It should be mentioned at the outset that hydroxylated compounds, which almost invariably give abnormally high values for viscosity, are not suitable for such a purpose; this point is apparent when the slope of the curves is considered, for whereas in Fig. 1 the log-viscosity-molecular-weight curves for such groups as paraffins,

ethers, esters, and ketones are parallel, it will be seen in Fig. 2 that the curve for the acids is by no means parallel with that for the carbinols. Further, as with almost every physical property, the results for the first one or two members of an homologous series tend to anomaly, and these should not be included.

FIG. 2.



Whilst employing our own determinations to support the thesis that log viscosity is an additive function, we have used chiefly the data of Thorpe and Rodger at 20° as a basis for the calculated values.

We have taken logarithms of viscosity $\times 10^5$ to avoid barred characteristics.

TABLE I.

Methylalkylcarbinols at 25° (Pickard and Kenyon).

	Viscosity.	$\text{Log } \eta \times 10^5$.	ΔCH_2 .
isoPropyl alcohol.....	0.0208	3.3189	0.0881
Methyl-n-propylcarbinol	0.0309	3.4901	0.1160
Methyl-n-butylcarbinol	0.0398	3.6001	0.1036
Methyl-n-amylcarbinol	0.0506	3.7037	0.1125
Methyl-n-hexylcarbinol	0.0655	3.8162	0.1018
Methyl-n-heptylcarbinol	0.0828	3.9180	0.0863
Methyl-n-octylcarbinol	0.1010	4.0043	0.0849
Methyl-n-nonylcarbinol	0.1228	4.0892	

TABLE II.

isoPropylalkylcarbinols at 25° (Pickard and Kenyon).

	Viscosity.	$\text{Log } \eta \times 10^5$.
Methylisopropylcarbinol	0.0351	3.5449
Ethylisopropylcarbinol	0.0403	3.6050
n-Propylisopropylcarbinol	0.0474	3.6761
n-Butylisopropylcarbinol	0.0709	3.8505
n-Amylisopropylcarbinol	0.0729	3.8629
n-Hexylisopropylcarbinol	0.1018	4.0077
n-Octylisopropylcarbinol	0.1431	4.1557

A marked abnormality in the fourth member (compare Pickard and Kenyon, *loc. cit.*) throws out the regularity of this series as a means of obtaining CH_2 values.

TABLE III.

Esters of the Oxalic Series at 25°.

	Viscosity.	$\text{Log } \eta \times 10^5$.	ΔCH_2 .
Diethyl oxalate	0.01751	3.2433	
" malonate	0.01875	3.2730	
" succinate	0.02400	3.3802	
" glutarate	0.02480	3.3945	
" adipate	0.02768	3.4425	
" pimelate	0.03280	3.5160	0.0899
" suberate	0.04034	3.6059	0.0994
" sebacate	0.05073	3.7053	

This series shows anomaly up to the glutaric member.

TABLE IV.

Fatty Acids at 20° (Gartenmeister).

	Viscosity.	$\text{Log } \eta \times 10^5$.	ΔCH_2 .
Formic acid.....	0.01804	3.2562	
Acetic ".....	0.01232	3.0906	
Propionic ".....	0.01107	3.0441	0.1595
Butyric ".....	0.01598	3.2036	0.1459
Valeric ".....	0.02236	3.3495	0.1553
Hexoic ".....	0.03201	3.5053	0.1333
Heptoic ".....	0.04356	3.6391	0.1205
Octoic ".....	0.05749	3.7596	0.1605
Nonoic ".....	0.08319	3.9201	

The Value for CH₂.

Substance.	η .	$\Delta \log \eta \times 10^5$ for CH ₂ .	
Hexane	0.00320	0.109	} 0.109 paraffins
Heptane	0.00411	0.117	
Octane	0.00538	0.102	
isoHexane	0.00300		
isoHeptane	0.00379		
Ethyl iodide	0.00583	0.102	} 0.102 alkyl iodides
Propyl "	0.00737		
isoPropyl iodide	0.00690	0.101	
isoButyl "	0.00870		
Methyl propyl ether	0.002515	0.101	} 0.108 ethers
Ethyl " "	0.003175		
Propyl " "	0.00420	0.128	
Ethyl " "	0.002345		
Propyl " "	0.00420	0.111	
Methyl propyl "	0.002515		
" isobutyl "	0.003065	0.092	
Ethyl " "	0.003785		
Ethyl acetate	0.00449	0.112	} 0.107 esters
Propyl "	0.00581		
Methyl propionate	0.00454	0.103	
" butyrate	0.00575		
Acetone	0.003225	0.096	} 0.106 ketones
Methyl propyl ketone	0.00501		
" ethyl "	0.00423	0.117	
Acetone	0.00501		
Propyl alcohol	0.0226	0.118	} 0.116 alcohols
Butyl "	0.0295		
isoButyl "	0.0391	0.115	
isoAmyl "	0.0509		
Methyl sulphide	0.00293	0.091	} 0.091 sulphides
Ethyl "	0.00455		

Mean value for 16 pairs = 0.107.

Value at 20° of $\log \eta \times 10^5$ for the Chief Groups.

CH₂ 0.107

Hydrogen.—Subtracting the CH₂ value from $\log \text{viscosity} \times 10^5$ of the paraffins, we get:

From hexane	0.931	} Mean for H = 0.934
" heptane	0.932	
" octane	0.938	

Alcoholic Hydroxyl.—Subtracting the value for CH₂ and H from the $\log \text{viscosity} \times 10^5$ of the higher alcohols, we get:

From propyl alcohol	2.097	} Mean for OH = 2.102
" butyl "	2.108	

Etheral Oxygen.—Subtracting the value for the alkyl radicles from the $\log \text{viscosity} \times 10^5$ of the ethers, we get:

From methyl propyl ether	0.105	} Mean for O = 0.098
" ethyl " "	0.099	
" propyl ether	0.113	
" ethyl "	0.074	

132 RELATION BETWEEN VISCOSITY AND CHEMICAL CONSTITUTION

Carbethoxyl.—Subtracting the value for the alkyl radicles from log viscosity $\times 10^5$ of the higher fatty esters, we get:

From ethyl propionate.....	1.583	} Mean for $\text{CO}_2\text{Et} = 1.573$
„ „ butyrate.....	1.570	
„ „ valerate.....	1.566	

Carbon.—Subtracting the value for hydrogen from that of CH_2 , we get $\text{C} = -1.761$.

Carbonyl (Ketonic).—Subtracting the value of the alkyl radicles from the log viscosity $\times 10^5$ of the ketone, we get:

From acetone.....	0.427	} Mean for $\text{CO} = 0.407$
„ methyl ethyl ketone	0.437	
„ „ propyl „	0.404	
„ diethyl ketone	0.372	

isoUnion.—Subtracting the value for the normal compounds from those of the *iso*-isomeride, we get:

From <i>isohexane</i> - hexane	-0.028	} Mean for <i>iso-union</i> = -0.030
„ <i>isheptane</i> - heptane	-0.035	
„ <i>isopropyl bromide</i> - propyl bromide...	-0.030	
„ <i>isopropyl iodide</i> - propyl iodide	-0.029	

Double Bond.—Subtracting the value for the saturated compound from those of the unsaturated body and two H values, we get:

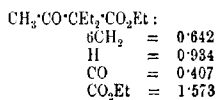
From allyl iodide + 2H - propyl iodide	1.862	} Mean for double bond 1.847
„ „ bromide + 2H - propyl bromide ...	1.850	
„ „ chloride + 2H - propyl chloride ...	1.840	
„ $\frac{1}{2}$ [diallyl + 4H - hexane]	1.835	

Collected Values at 20°.

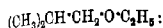
CH_2	0.107	O (etheral)	0.093
H	0.934	CO_2Et	1.573
OH (alc.)	2.102	C	-1.761
CO (ketonic)	0.407	<i>iso-union</i>	-0.030
Double bond	1.847		

The following examples of the synthesis of a molecular value may be given:

(1) *Ethyl Diethylacetoacetate*. $\eta_{sp} = 0.0344$ (Gartenmeister).



$$3.556 = \log \text{ of } 6.0360 \times 10^5$$

(2) *isoButyl Ether*. $\eta_{sp} = 0.0376$ (Thorpe and Rodger).

$6CH_2 = 0.642$

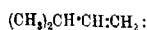
$O = 0.093$

$2H = 1.868$

$\hline 2.608$

$iso = -0.030$

$\hline 2.578 = \log \text{ of } 0.0376 \times 10^5$

(3) *isoAmylene*. $\eta_{sp} = 0.00212$ (Thorpe and Rodger).

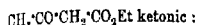
$5CH_2 = 0.535$

$: = 1.847$

$\hline 2.382$

$iso = -0.030$

$\hline 2.352 = \log \text{ of } 0.00225 \times 10^5$

(4) *Ethyl Acetoacetate*. $\eta_{sp} = 0.0168$ (Gartenmeister).

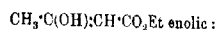
$2CH_2 = 0.214$

$H = 0.934$

$CO = 0.407$

$CO_2Et = 1.573$

$\hline 3.128 = \log \text{ of } 0.0134 \times 10^5$



$2CH_2 = 0.214$

$OH = 2.102$

$CO_2Et = 1.573$

$: = 1.847$

$\hline 5.736$

$C = -1.761$

$\hline 3.975 = \log \text{ of } 0.0944$

Therefore, percentage of enolic form = 4.2.

Knorr (*Ber.*, 1911, **31**, 1138, 2767) finds 2 per cent. of enol, and Meyer (*Annalen*, 1911, **380**, 212) obtained 7.5 per cent. of enol, a value confirmed by Hantzsch (*Ber.*, 1910, **30**, 49).

In this preliminary communication it must be pointed out that the amount of available data is not sufficient to admit of very satisfactory values being deduced. We hope to examine in the near future a large number of homologous series at a variety of temperatures, so as to amass enough experimental material to render possible the compilation of trustworthy constants.

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XX.—The Relation between Viscosity and Chemical Constitution. Part VII. The Effect of the Relative Position of Two Unsaturated Groups on Viscosity.

By ALBERT ERNEST DUNSTAN, THOMAS PERCY HILDITCH, and
FERDINAND BERNARD THOLE.

DURING OUR examination of the influence of various constitutive features on the viscosity of organic compounds, the results of which *Zeitsch. Elektrochem.*, 1911, **17**, 929; 1912, **18**, 185) have so far

served to correlate that essentially constitutive property with other physical characteristics already studied by previous workers, we have felt that, more particularly as regards the anomalous effects of "unsaturation," the numerous investigations of the past few decades have given but little insight into the underlying causes. It appeared to us that a more detailed study of the mutual influence of two unsaturated groups which are not chemically united in the molecule, but which exert definite effects, either chemical or physical, apparently owing merely to their spatial proximity, might possibly lead further in the desired direction.

We have therefore extended our work on the general correlation of viscosity with other physical properties by examining the viscosities of the members of a number of homologous series of compounds containing two unsaturated groups at varying degrees of proximity to each other.

Instances of effects due to "spatial conjugation," as it has been termed, have not hitherto been met with at all frequently in physico-organic chemistry, although many cases of intramolecular chemical change supposedly due to the nearness in space of the reacting groups will be recalled. Refractivity, one of the most thoroughly studied properties, seems to be insufficiently constitutive to respond to any spatial influences (these, it may at once be said, are in general of a much smaller order than those due to ordinary conjugation), and although optical activity is affected by them (Hilditch, T., 1909, **95**, 1578; *Zeitsch. physikal. Chem.*, 1911, **77**, 482), too little is yet known of the general rules which govern the relation between conjugated unsaturation and molecular rotatory power to permit of any extension of these to the present case. Clarke has, however, shown that spatial proximity and reactivity of unsaturated atoms are connected (T., 1911, **99**, 1927; 1912, **101**, 1788).

As regards the changes in viscosity due to varying constitution, it may be said in general that viscosity is lowered by molecular symmetry, but enhanced by single (and still more by conjugated) unsaturation, by symmetrical conjugation, and by molecular association.

The following illustrations may be given of these general rules:

Molecular Symmetry.—The figures for some isomeric primary, secondary, and tertiary amines (Mussell, Thole, and Dunstan, T., 1912, **101**, 1008) show the rapid diminution of viscosity with increasing symmetry of the molecule:

	$\eta \times 10^6$
	Mol. vol.
n-Butylamine	70.8
Diethylamine	36.2
(Triethylamine	26.1)

The general result that substitution of a hydrogen atom by an alkyl group lowers the molecular viscosity is also due probably to the increased symmetry of the alkylated compound.

Simple unsaturation, on the other hand, induces a distinct increase in the value of the expression $\frac{\eta \times 10^6}{\text{Mol. vol.}}$, as is typified by such data as the following:

	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$
Ethyl <i>n</i> -propyl ether.....	29.4
Ethyl propargyl ether	52.2

The effect of *conjugated unsaturation* is much more marked; thus we quote:

Acetone	66.9
Mesityl oxide	84.0
Phorone	90.6
Safrole	155.1
<i>iso</i> -Safrole (conjugated)	274.2

These figures also illustrate the fact that in cases where the conjugated systems form a symmetrical grouping the effect due to any simple molecular symmetry is not only masked, but of itself the *symmetrical conjugation* produces an effect greater than that due to ordinary conjugation (compare mesityl oxide and phorone).

Attention must also be drawn to the fact that the presence of groups which promote molecular association causes an enormously magnified exaltation of molecular viscosity; for example, eugenole, safrole, *isoeugenole*, and *isosafrole* are corresponding allyl and propenyl derivatives of catechol ethers, the only difference being that the eugenoles contain a methyl and an hydroxyl group, the safroles a methylenedioxy-radicle; nevertheless, the hydroxyl group causes a most enormous increase in molecular viscosity:

	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$
Eugenole	448.5
<i>iso</i> -Eugenole.....	1759.0

Finally, it is interesting to note the enhancing influence of a symmetrical arrangement of unsaturated radicles around a central atom:

Aniline.....	55.1
Diphenylamine	61.1
Triphenylamine	262.0
Benzylamine	37.0
Dibenzylamine	39.5
Tribenzylamine	69.9

Bearing in mind, then, these various well-defined constitutive influences, we proceed to the results of our present work on some

simple cases of spatial conjugation of unsaturated groups. All the series enumerated in this communication may be represented by the general formula $R \cdot [CH_2]_n \cdot R'$, R and R' being either the same or different unsaturated radicles, so that the compounds studied were disubstituted normal paraffins.

EXPERIMENTAL.

Our methods and apparatus remained the same as those described in earlier papers; the experimental material was in some instances purchased from Schuchardt or Kahlbaum, and repurified by distillation or crystallisation, but in the majority of cases we prepared the necessary compounds by methods which, being adapted from current literature, need not be further detailed. Unfortunately, a few of the more interesting substances proved so exceedingly difficult to prepare in the necessary quantities that we had perforce to omit them; this was notably the case with the $\alpha\delta$ -dihalogen derivatives of butane. In some other series it was found impracticable to proceed beyond the fourth or fifth member, but the result of an extended series of esters of the normal dicarboxylic acids would appear to indicate that it is only in the lower members that the anomalies which are the primary object of our research present themselves to any marked extent.

Series containing Two Identical Unsaturated Radicles.

TABLE I.

Diethyl Esters of Normal Aliphatic Dicarboxylic Acids at 25°.

We have measured the viscosities of the members of this series from diethyl oxalate to diethyl sebacate, and our mean results are as follows:

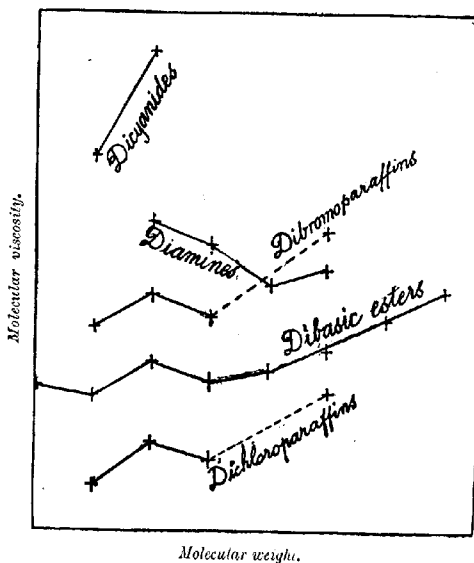
	D_{20}^{25} .	η_{20}^{25} .	$\eta \times 10^5$ Mol. vol.
Diethyl oxalate	1.0725	0.01751	128.5
„ malonate	1.0501	0.01875	123.2
„ succinate	1.0362	0.02399	142.9
„ glutarate	1.0185	0.02479	132.0
„ adipate	1.0110	0.02768	137.9
„ pimelate	0.9929	0.03279	150.7
„ suberate	0.9951	0.04036	172.6
„ sebacate	0.9812	0.05073	188.6

It is evident from the appended curve (Fig. 1) that the viscosities lie on a smooth curve, with the exception of the oxalic and succinic derivatives. The enhanced value for the first member was to be anticipated from our former work on the influence of ordinary conjugation on viscosity; the anomalous figure for the succinic ester must be ascribed to the effect of spatial conjugation, and as appears from the remaining series of this type reported on, this is

a general feature of the viscosities of the compounds of the general type $R \cdot CH_2 \cdot CH_2 \cdot R$. It is almost unnecessary to point out that it is this type of substance in which the chemical effects of spatial conjugation (such as elimination of water to form anhydrides, etc.) are most prominent.

The optical activity of the dimethyl esters of the same series of acids has been shown by one of us (*loc. cit.*) to exhibit similar anomalies due to spatial effects, but, curiously enough, in the latter case the enhanced value does not appear until the adipic ester, in.

FIG. 1.



which the carboxylic groups as a whole, rather than their hydroxylic (or alkylic) components, may be supposed from the usual steric hypotheses to be nearest to one another in space.

TABLE II.

Alkylene Dichlorides at 25°.

	D_4^{25} .	η_{25}^0 .	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$
Methylene dichloride	1.3055	0.004413	67.7
Ethylene dichloride	1.2525	0.007495	94.5
Trimethylene dichloride	1.1770	0.008697	90.6
Pentamethylene dichloride,	1.0940	0.015947	123.8

TABLE III.

Alkylene Dibromides at 25°.

	D_4^{25}	η^{25}	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$
Methylene dibromide.....	2.4080	0.01225	165.0
Ethylene dibromide	2.1620	0.01605	184.5
Trimethylene dibromide	1.9380	0.01790	171.7
Pentamethylene dibromide	1.6940	0.03040	224.0

TABLE IV.

Alkylene Diamines at 25°.

Ethylenediamine	0.898	0.0154	230.0
Trimethylenediamine.....	0.884	0.0180	216.0
Tetramethylenediamine.....	0.877	0.01915	191.0
Pentamethylenediamine	0.873	0.02350	201.0

We also compared the viscosities of malono- and succino-nitriles at 60°; the value for the former is derived by extrapolation from Walden's figures (*Zeitsch. physikal. Chem.*, 1912, **79**, 717), whence

D_4^{60} 1.024, η^{60} 0.0175, so that $\frac{\eta \times 10^6}{\text{Mol. vol.}} = 271$. Our measurements

of the viscosity of succinonitrile were:

Temperature.	D_4^t	η^t
53.7°	0.989	0.0276
69.4	0.9805	0.0236
83.0	0.9765	0.0181

from which $\eta \times 10^6/\text{Mol. vol.}$ at 60° is 336.

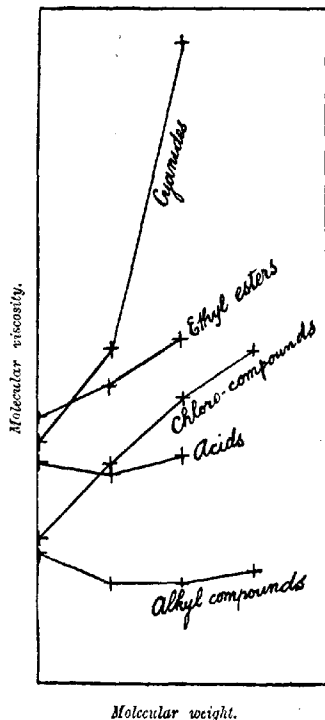
The values throughout these further series are accordingly of the same nature as those of the dibasic esters. Of course, in these instances the first terms of each series (corresponding with diethyl oxalate) are compulsorily omitted, namely, the elements chlorine and bromine, and the compounds cyanogen and hydrazine. We commence, therefore, at the terms corresponding with diethyl malonate, and find that the molecular viscosity rises in the next member, the ethylene compound corresponding with diethyl succinate, then falls in the cases of the trimethylene derivatives, and finally, so far as can be judged from the values for the tetra- and penta-methylene compounds, appears to rise steadily with ascending molecular weight in precisely analogous fashion to those of the remainder of the dibasic esters.

The curve for the diamines accentuates the anomaly noticeable in the preceding series, a fact which, in common with certain other results which follow, emphasises the unusually great influence which the amino-complex, like the hydroxyl radicle, exerts on viscosity.

There remains established the existence of similar anomalies in

each of these series of compounds, anomalies, moreover, which occur at that term of the homologous series at which accepted steric considerations show the unsaturated groups to be in unusually close spatial proximity.

FIG. 2.



Series in which the Two Unsaturated Groups are Different
 ($R = C_6H_5$; $R' = Cl, CO_2H, CO_2Et, NH_2, CN, \text{ or } OH$).

For the sake of comparison we have added here the viscosities of some of the phenyl paraffins of analogous structure to their unsaturated substituents, which we deal with subsequently.

TABLE V.

Alkylbenzenes at 25°.

	D_4^{25}	η^{25}	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$
Benzene	0.873	0.00601	67.3
Toluene.....	0.860	0.00548	51.2
Ethylbenzene	0.862	0.00630	51.2
n-Propylbenzene	0.859	0.00790	56.6

TABLE VI.

Monochloroalkylbenzenes at 25°.

Chlorobenzene.....	1.103	0.00758	74.3
Benzyl chloride	1.100	0.0128	111.5
β -Chloroethylbenzene.....	1.069	0.0191	145.0
γ -Chloro-n-propylbenzene	1.056	0.0246	168.0

TABLE VII.

Ethyl Esters of the Homologous Benzoic Acids at 25°.

Ethyl benzoate	1.041	0.01956	136.0
Ethyl phenylacetate	1.029	0.02386	150.0
Ethyl β -phenylpropionate	1.014	0.03060	175.0

The viscosities of the corresponding acids were also measured at 130°, and at a degree higher than their respective melting points. The data show that the values at 130°, as would be expected, are much smaller than the values which would be obtained if it were possible to supercool the acids to 25°. Unfortunately, owing to the large and non-linear temperature-coefficient, it was impossible to attempt any extrapolation of the data to 25°.

TABLE VIII.

Homologous Benzoic Acids.

	Temp.	D_4^T	η^T	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$
Benzoic acid	130.0°	1.078	0.0126	112
	122.5	1.080	0.0167	146
Phenylacetic acid	130.0	1.043	0.0140	107
	77.0	1.091	0.0354	283
β -Phenylpropionic acid ...	130.0	1.023	0.0172	116
	49.7	1.047	0.0979	663

TABLE IX.

Nitriles of the Homologous Benzoic Acids at 25°.

	D_4^{25}	η^{25}	$\frac{\eta \times 10^6}{\text{Mol. vol.}}$
Benzonitrile	1.003	0.0125	122
Phenylacetonitrile	1.015	0.0197	170
β -Phenylpropionitrile	1.079	0.0477	322

Walden (*Zeitsch. physikal. Chem.*, 1911, **78**, 275) has recorded the absolute viscosities of benzonitrile and phenylacetone nitrile as 0.0122 and 0.0193 respectively at 25°.

TABLE X.

Homologous Amines of the Benzene Series at 25°.

	D_{20}^{20} .	η_{25}^{25} .	$\frac{\eta \times 10^4}{\text{Mol. vol.}}$
Aniline	1.018	0.03740	410
Benzylamine	0.9812	0.01596	146
β -Phenylethylamine	0.9640	0.02490	198
γ -Phenyl- <i>n</i> -propylamine ...	0.9760	0.03570	240

Finally, we examined the similar series of homologous hydroxyl compounds at 25° and at 50°:

TABLE XIa.

Phenol and Phenylalkyl Alcohols at 25°.

Phenol	1.070	0.0850	968
Benzyl alcohol	1.045	0.05285	511
β -Phenylethyl alcohol	1.023	0.07580	634
γ -Phenyl- <i>n</i> -propyl alcohol	0.995	0.156	1060

TABLE XIb.

The Same Compounds at 50°.

Phenol	1.052	0.0337	377
Benzyl alcohol	1.029	0.0260	248
β -Phenylethyl alcohol	1.003	0.0319	262
γ -Phenyl- <i>n</i> -propyl alcohol	0.972	0.0521	373

A comparison of these results with the preceding discloses at once certain resemblances and a number of marked differences, and is facilitated by the accompanying curve.

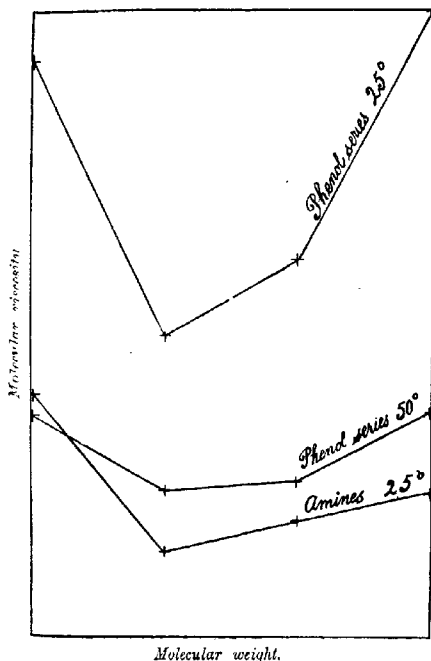
In the first place, if we confine attention in both classes of compounds—symmetrically and non-symmetrically substituted—to those series which have an unsaturated group in common, it is obvious that the general order of the viscosities at 25°, as exemplified by the relative positions of the corresponding curves, is the same for the chloro-, carboxy-, amino-, and cyano-derivatives. In addition, in the aromatic (non-symmetrically disubstituted) series, the curve connecting the viscosities of the corresponding aromatic hydrocarbons (in which compounds the second unsaturated radicle is replaced by a hydrogen atom) is beneath all the related curves. In other words, the order in which the curves arrange themselves in each of the two groups is not only the same, but is also approximately that of increasing unsaturation of the second unsaturated residue (R'), so far as can be judged from a general survey of the

usual physical and chemical characteristics conferred on compounds by the substituents in question.

Moreover, in general, the first member of the series, containing two chemically adjacent unsaturated groups, possesses an enhanced viscosity compared with the values for the remaining members of the series.

Here, however, the resemblance between the two groups of curves

FIG. 3.



ends, and further consideration of the aromatic group shows that the latter arrange themselves in two divisions:

(a) Those series which show a marked exaltation for the first (conjugated) member, namely, the hydroxy-, amino-, cyano-compounds and esters.

(b) In the second division of the aromatic series, which comprises the chloro- and hydrocarbon groups, no measurable depression occurs at the second member, and this is not unnatural, since, whilst the chlorine atom in organic compounds is generally supposed

to possess but little residual affinity, the hydrocarbons contain no second unsaturated residue at all, and consequently the effects of conjugation are at a minimum in both cases.

Regarding the question in this light, and bearing in mind the general behaviour of compounds containing chemically adjacent unsaturated groups, it is natural to suppose that the separation of these groups leads to a falling off in any enhancing effect, but that such exalting influences again become apparent as the unsaturated residues gradually reapproach each other in space. It would have been most interesting to have examined the higher members in each series, but, as is well known, most of these have yet to be synthesised, whilst the difficulties of preparation and purification of the few which are known increase out of all proportion to their molecular weight.

Nevertheless, we are able to point out the following consistent effects caused by the replacement of hydrogen by chlorine, the carbethoxy-group, the cyano-, amino-, and hydroxyl-residues on the curves connecting the viscosities of the members of the various homologous series:

(i) The relative positions of the curves are in the order given, that is, with one or two exceptions discussed below, the general order of increasing unsaturation of the second unsaturated group.

(ii) The slope of each curve is roughly determined by its relative position, and increases progressively as the second substituent becomes less saturated.

(iii) Correspondingly, the magnitude of the depression at the second member increases on passing up the series of curves in exactly the same order.

Most remarkable, however, is the fact that the well-defined exaltation characteristic of the substances of the general formula $R \cdot CH_2 \cdot CH_2 \cdot R$ is totally absent in the aromatic series we have studied. Two possible explanations suggest themselves in this connexion: from steric considerations it is likely that in view of the greater mass of the phenyl group the remaining (smaller) unsaturated radicle is not in the same spatial position with regard to that group in the compound $R \cdot CH_2 \cdot CH_2 \cdot Ph$ as the two (small) unsaturated residues are to each other in the symmetrical compounds $R \cdot CH_2 \cdot CH_2 \cdot R$. Another possibility raises the whole question of the mutual influence of two identical as compared with that of two different unsaturated radicles; is it possible that two identical unsaturated radicles, spatially proximate in the same molecule, should exert an exalting effect on a physical property, whilst two dissimilar unsaturated groups in the same relative configurations may depress the values for the same property?

Some recent work by Clarke (T., 1912, 101, 1801) lends support to the supposition that such may be the case, for this author finds that the reactivity of compounds of the type $X \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} Y$, where X and Y are two atoms possessing residual affinity, is promoted when X and Y are the same, but decreased when these are atoms of different elements.

General Conclusions.

(1) We have examined the viscosities of a number of homologous series of compounds of the respective types $R \cdot [CH_2]_n \cdot R$ and $Ph \cdot [CH_2]_n \cdot R$, where R is a varying unsaturated radicle.

(2) In both series the general order of the molecular viscosity rises when R is varied in the order: chloro-, carbethoxy-, amino-, and cyano-radicles.

(3) In both series the initial member, containing two chemically adjacent unsaturated groups, has been found to possess an exalted molecular viscosity.

(4) In the symmetrical series $R \cdot [CH_2]_n \cdot R$ the members represented by $R \cdot CH_2 \cdot CH_2 \cdot R$ possess an enhanced value for $\frac{\eta \times 10^6}{\text{Mol. vol.}}$, but this is not the case in the phenyl group of compounds.

(5) In the latter group of compounds the anomaly of the initial member is in general very pronounced, and is followed by an equally well-marked depression in the case of the viscosity of the second member, the values thereafter rising somewhat rapidly; the extent of the depression, the relative slope of the curves, and the relative positions of the curves are in the order: chloro-compounds, esters, amino-, cyano-, and hydroxy-compounds.

(6) The series examined afford undoubted evidence of the strong mutual influence of two unsaturated groups upon viscosity, not only when the radicles concerned are adjacent in the molecule, but also when they may be supposed from common steric considerations to approach one another in space.

(7) In addition, we have obtained indications of the varied influences exerted by combinations of two similar, and, on the other hand, of two dissimilar radicles, the effects in the latter case depending to all appearance on the relative degree of unsaturation of the component radicles; our data, however, do not permit us to define the latter variations more particularly.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

	PAGE
XXI.—An Attempt to Harmonise, Qualitatively, the Relation between Temperature and Rotation for Light of all Refrangibilities of Certain Active Substances, both in the Homogeneous State and in Solution. By THOMAS STEWART PATTERSON	145
XXII.—Quinone-ammonium Derivatives. Part II. Nitrohaloid, Dibaloid and Azo-compounds. By RAPHAEL MELDOLA and WILLIAM FRANCIS HOLLELY	177
XXIII.—The Constituents of the Rhizome and Roots of <i>Caulophyllum thalictroides</i> . By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY	191
XXIV.—Quercetagenin. By ARTHUR GEORGE PERKIN	209
XXV.—The Chlorination of Iodophenols. Part II. The Chlorination of <i>o</i> -Haloid Derivatives of <i>p</i> -Iodophenol. By GEORGE KING, M.Sc. (Priestley Research Scholar of the University of Birmingham), and HAMILTON MCCOMBIE	220
XXVI.—2 : 2'-Ditolyl-5 : 5'-dicarboxylic Acid. By JAMES KENNER and ERNEST WITHAM	232
XXVII.—The Action of Ammonia and Alkylamines on Reducing Sugars. By JAMES COLQUHOUN IRVINE, ROBERT FRASER THOMSON, M.A., B.Sc., and CHARLES SCOTT GARRETT, B.Sc.	238
XXVIII.—The Form of Extinction Curves: Cobalt Nitrate Solutions. By THOMAS RALPH MERTON, B.Sc. (Oxon.)	249
XXIX.—The Influence of Water on the Partial Pressures of Hydrogen Chloride above its Alcoholic Solutions. By WILLIAM JACOB JONES, ARTHUR LAPWORTH, and HERBERT MUSCHAMP LINGFORD	252
XXX.—The Presence of Helium in the Gas from the Interior of an X-Ray Bulb. By Sir WILLIAM RAMSAY, K.C.B.	264

	PAGE
XXXI.—Vaubel's Supposed Phenyl-di-imine. By MARTIN ONSLOW FORSTER and JOHN CHARLES WITHERS	266
XXXII.— $\alpha\delta$ -Derivatives of Adipic and β -Methyladipic Acids, and the Preparation of Muconic and β -Methylmuconic Acids. By HENRY STEPHEN and CHARLES WEIZMANN	269
XXXIII.—The Chemistry of the Glutaconic Acids. Part VII. The Normal and Labile Forms of $\alpha\gamma$ -Dimethylglutaconic Acid and their Reduction to <i>cis</i> - $\alpha\gamma$ -Dimethylglutaric Acid. By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD	276
XXXIV.—The Measurement of Tryptic Protein Hydrolysis by Determination of the Tyrosine Liberated. By SAMUEL JAMES MANSON AULD and THOMAS DUNCAN MOSSCROP, B.Sc.	281
XXXV.—The Solubility of Sulphanilic Acid and its Hydrates. By JAMES CHARLES PHILIP	284
XXXVI.—The Alkaloids of <i>Xanthoxylum brachyacanthum</i> . By HOOPER ALBERT DICKINSON JOWETT and FRANK LEE PYMAN	290
XXXVII.—The Precipitation of Lead Thiosulphate and its Behaviour on Boiling with Water. By WILLIAM HUGHES PERKINS and ALBERT THEODORE KING	300
XXXVIII.—Ionisation and the Law of Mass Action. By WILLIAM ROBERT BOUSFIELD, M.A., K.C.	307

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:—

PART I.

Organic Chemistry.

KISHNER (NICOLAI M.). Purification of Saturated Hydrocarbons by means of Potassium Permanganate	i, 153
VIGNON (LÉO). Fractional Distillation of Coal	i, 153
JEGOROV (JOH.). A New Method for Determining the Position of the Double Bond	i, 153
MOHR (ERNST). The Theory of the Asymmetric Carbon Atom and Pasteur's Principle	i, 155
BIRON (EUGEN VON). The Melting Point of Ethylene Dibromide	i, 155
LIPPMANN (EDMUND O. VON). The History of Distillation and of Alcohol	i, 155
BASKERVILLE (CHARLES). Ethyl Ether by Catalysis	i, 155
LANGHELD (KURT), F. OPPMANN, and E. MEYER. Esters and Amides of the Phosphoric Acids. IV. Reaction between Esters of Metaphos- phoric Acid and Uni- and Multi-valent Alcohols. Synthesis of Glycero- mono- and -diphosphoric Acid. Preparation of Pure Silver Meta- phosphate	i, 155
CARRÉ (PAUL). The Glycerotriphosphoric Acid of Contardi	i, 156
BLEICHER (K.). Crystalline Forms of Salts of Ethanedisulphonic Acid	i, 156
SMITS (ANDREAS) and S. C. BOEHORST. Phenomenon of Double Melting for Fats	i, 157

CONTENTS.

iii

	PAGE
GRÜN (ADOLF) [with A. CUSTODIS]. Anomalies in the Consistency and Melting Points of Fats	i, 157
HOLDE (DAVID). The Synthesis of Fats	i, 158
GRÜN (ADOLF) and FRITZ KADE. Diglyceride-phosphoric Acids	i, 158
GRÜN (ADOLF) and FRITZ KADE. Alleged Synthesis of Lecithins	i, 158
GRÜN (ADOLF) and B. SCHREYER. Preparation of Mixed $\alpha\beta$ -Diglycerides	i, 159
ELSDON (GEORGE D.). Alcoholysis and the Composition of Coconut Oil	i, 159
TROBRIDGE (FREDERICK G.). Preparation of Ethyl Acrylate	i, 160
BUNGE (NICOLAI N.). Action of Zinc on a Mixture of Pinacolin and Ethyl α -Bromopropionate	i, 160
MAZZUCHELLI (ARRIGO) and OLGA GRECO D'ALCEO. Uranium Salts	i, 160
NOTES (WILLIAM A.) and LEONIDAS R. LITTLETON. Molecular Rearrangements in the Camphor Series. XI. Derivatives of <i>iso</i> Camphoric Acid: <i>iso</i> Aminocamphonic Acid and its Decomposition Products	i, 161
BRENT (JULIUS) [and, in part, PAUL LEVY and S. LINK]. New Methods of Preparation of Camphonic (γ -Lauronic) Acid and the Relation of the Latter to Lauronic (Lauronic) Acid	i, 162
BRENT (JULIUS) and AUGUST AMANN. A New Method of Preparation of Lauronic (Lauronic) Acid and the Decomposition of Camphonic Acid in an Electric Reflux Heater under Diminished Pressure	i, 162
BELL (JAMES M.) and CHARLES F. COWELL. Methods for the Preparation of Neutral Solutions of Ammonium Citrate	i, 162
FRIES (KARL) and H. MENGEL. Thio- γ -valerolactone	i, 163
WOHL (ALFRED) and BRUNO MYLO. Maleindialdehyde	i, 163
MICHAELIS (LEONOR) and PETER RONA. The Isomeric Changes of Dextrose Produced by Alkalis. Theory of Catalytic Action	i, 164
FISCHER (EMIL) and KARL ZACH. Conversion of <i>d</i> -Glucose [Dextrose] into a Methylpentose	i, 164
EGOROV (M. A.). Properties of Phytin	i, 165
MAILLARD (LOUIS C.). Formation of Humus and Combustible Minerals without the Intervention of Atmospheric Oxygen, Micro-organisms, High Temperatures, or Great Pressure	i, 165
SCAGLIARINI (GINO). Some Unstable Nitrites Fixed by means of Organic Bases. III.	i, 166
EILTZ (HEINRICH) [with E. TOPP and J. KARTTE]. Alloxan Anhydride and Its Methyl Derivatives	i, 166
SMITS (ANDREAS) and A. KETTNER. The System Ammonium Thiocyanate-Thiocarbamide-Water	i, 167
ZEMINSKI (NICOLAI D.) [with W. DOBROCHOTOV and (Frl.) A. HERZENSTEIN]. Selective Catalysis of Dehydrogenation	i, 167
HALLER (ALBIN) and EDOUARD BAUER. Formation of Dimethylstyrene [<i>S</i> -Phenyl- Δ^6 -butylene] from Phenyl-dimethylethyl Alcohol [<i>S</i> -Phenyl- <i>isobutyl</i> Alcohol]	i, 168
JACKSON (C. LORING) and WEBSTER N. JONES. 2:4:6-Tribromo-1-iodo-3-nitrobenzene	i, 168
HOLLEMAN (ARNOLD F.) and J. P. WIBAUT. The Nitration of the Chlorotoluenes	i, 169
TROGER (JULIUS) and W. KROSEBERG. $\alpha\alpha$ -Dihalogenoarylsulphonylacetone-nitriles, $R\cdot SO_2\cdot CX_2\cdot CN$, and a Peculiar Reduction of these Halogen Compounds	i, 169
MASCARELLI (LUIGI). Spontaneous Formation of Iodonium Bases Containing Iodine in a Pentatomic Heterocyclic Nucleus	i, 171
BOESCHE (WALTHER) and J. WOLLEMAN. $\omega\omega'$ -Diarylated Aliphatic Hydrocarbons	i, 171
ODELL (ALLAN F.) and CLEVE W. HINKS. Pyrosulphates of Sodium and Potassium as Condensing Agents	i, 172
MAILHE (ALPHONSE). Nitro-derivatives of <i>m</i> -Cresyl Oxide [<i>m</i> -Tolyl Ether]	i, 173
EVANS (WM. LLOYD) and LOU HELEN MORGAN. Preparation and Oxidation of Styrolene Alcohol [Phenylethylene Glycol]	i, 173

	PAGE
SMYTHE (JOHN A.). Preparation of Benzyl Mercaptan	i, 174
FROMM (EMIL), HANS BENKINGER, and FRITZ SCHÄFER. Derivatives of Ethylene Dimercaptan, $\text{SH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SH}$, <i>s</i> -Dithiolethylene, $\text{SH}\cdot\text{CH}=\text{CH}\cdot\text{SH}$, and of Dithiolactylene, $\text{SH}\cdot\text{CH}=\text{C}(\text{SH})\cdot\text{SH}$	i, 174
FROMM (EMIL) and AQUILA FORSTER [with MAX KLINGER]. Decomposition of Benzyl Disulphide by Alkalis	i, 175
FROMM (EMIL), AQUILA FORSTER, and BORIS VON SCHENKOWITZKI. Some Mercaptals and Mercaptols and their Derivatives	i, 176
ZELINSKI (NICOLAI D.) and N. UKLONSKAJA. Catalysis of Dehydrogenation of Hexahydrobenzoic [<i>cyclohexanecarboxylic</i>] Acid	i, 176
MADINAVEITIA (ANTONIO) and JOSÉ SUREDA BLANES. Study of Double Linkings	i, 177
ROBSON (S.). Some Para-derivatives of Phenylacetic Acid	i, 177
FISCHER (EMIL). Walden's Inversion and Substitution Processes. II.	i, 177
STORBE (HANS) [and NICOLAUS BARBASCHINOV]. Behaviour Towards Light of Cinnamylidenecetonitrile, of α -Phenylcinnamylidenecetic Acid, and of the two Cinnamylidenecetic Acids	i, 177
BELLUCCI (ITALO). Some Pharmaceutical Incompatibilities of Salol [Phenyl Salicylate]	i, 179
KÖTZ (ANTHON), K. BLENDERMANN, and J. MEYER. Condensation of Cyclic Ketones with Ethyl Oxalate	i, 179
BIDDLE (HENRY C.). Melting Point of Ethyl Gallate	i, 179
YABUTA (T.). Kojic Acid, a New Organic Acid Formed by <i>Aspergillus oryzae</i>	i, 180
FISCHER (EMIL) and HERMANN STRAUSS. Synthesis of β -Glucosidogallic Acid	i, 180
NIERENSTEIN (MAXIMILIAN) and FREDERIC W. RIXON. Some Reduction Products of Ellagic Acid	i, 180
ACKERMANN (DANKWART). New Basic Component of the Muscle of the Dog and its Relation to Hexamethylornithine	i, 181
GODCHOT (MARCEL) and FÉLIX TABOURY. The Bromination of <i>cyclopentanone</i>	i, 181
TABOURIECH (P. JOSEPH). 2:2-Dimethylcycloheptanone	i, 181
GODCHOT (MARCEL) and FÉLIX TABOURY. Electrolysis of <i>cyclopentanone</i>	i, 182
WALLACH (OTTO) and WOLFGANG VON RECHENBERG. Terpenes and Etheral Oils. CXII. Condensation Products of Cyclic Ketones and Acetone	i, 182
HALE (WILLIAM J.) and LAMBERT THORP. Studies in the <i>cyclopentadiene</i> Series. II. 5-Nitro-2:3-dibenzoylcyclopentadiene	i, 184
FROMM (EMIL) [with FRITZ HAAS and EMIL HUBERT]. Thio-derivatives of Ketones	i, 184
FROMM (EMIL) and JULIUS FLASCHEN. Stereoisomerism of Derivatives of Phenacyl Sulphide	i, 186
KISHNER (NICOLAI M.). Transformations of Thujone. II.	i, 187
PADOA (MAURIZIO) and G. ROTONDI. A Special Case of Racemism	i, 188
SEMMLER (FRIEDRICH W.) and FELIX RISSE. The Constituents of Essential Oils (The Constitution of Seline)	i, 188
NELSON (E. K.). Chemical Investigation of the Oil of Chenopodium. II.	i, 189
PEACHEY (STANLEY J.). Action of Gaseous Oxygen on Caoutchouc	i, 190
BEADIE (CLAYTON) and HENRY P. STEVENS. The Nitrogenous Constituent of Para Caoutchouc and its Bearing on the Nature of Synthetic Caoutchouc	i, 190
SPENCE (DAVID) and C. A. WARD. Chemistry of Caoutchouc. VI. Theory of Vulcanisation. IV.	i, 191
BENARY (ERICH). The Action of Chloroacetyl Chloride on Ethyl Malonate; Iminotetroneic Acid	i, 191
ANGELICO (FRANCESCO) and A. COPPOLA. Hydroxymethylfurfuraldehyde	i, 192
THOMS (HERMANN) and E. BAETCKE. Constitution of Bergapten	i, 192
LANSFRY (MAURICE). Action of Hydrogen Peroxide on Hydroxythionaphthen, Hydroxythionaphthen Carboxylic Acid, and "Thioindigo"	i, 193

CONTENTS.

v

	PAGE
FRIEDLAENDER (PAUL) and ST. KIELBASINSKI. "Bisphenylthiophen-indigo" [5:5'-Diphenyl-Δ ² -bisthiophen-8-one]	i, 193
ENGELAND (L. B.) and FRIEDRICH KUTSCHER. Methylation of Histidine, Arginine, and Lysine	i, 194
LEUCHS (HERMANN) and GEORGE PEIRCE. Strychnos Alkaloids. XVI. Dihydrobrucinic Acid and isoBrucinolone	i, 194
LEUCHS (HERMANN) and JOHANNES WUTKE. Strychnos Alkaloids. XVII. Isolation of the Hydrate of a Fourth Strychninesulphonic Acid	i, 195
PILOTY (OSKAR) and A. BLÖMER. Synthesis of Hæmopyrrole-δ	i, 196
BRAUN (JULIUS VON) and A. SCHMATLOCH. Cyclic Imines. VII. Ahrens' So-called γ-Picoline	i, 196
SCHÜTTE (JOH.). The Action of Hydroxylamine and Phenylhydrazine on Benzoyldahydracetic Acid. A Correction	i, 197
BRAUN (JULIUS VON) and B. BARTSCH. Cyclic Imines. VI. Ring Homologues of Tetrahydroquinoline	i, 197
WALTHER (REINHOLD VON) and H. ROCH. Thiazoles	i, 198
KISCHNER (NICOLAI M.) Decomposition of Alkylidenhydrazines	i, 203
JOHNSON (TREAT B.) Hydantoins. XX. Action of Thiocyanates on α-Amino-acids	i, 203
FROMM (EMIL) [with WILHELM BITTERICH]. Tetraphenyldi-iminotetrahydromiazthiole (3:5-Diphenylimino-1:4-diphenyltetrahydro-1:2:4-thiodisazole)	i, 204
MEYER (HANS) and KARL STEINER. Trimethylparamide	i, 204
FROMM (EMIL) [and RICHARD HEYDER, ADOLF JUNG, and MARGRET STURM]. Disulphides with Neighbouring Double Linkings. Derivatives of Dithiobiurets and of Thiores	i, 204
ROBATTI (ARISTIDE). Crystallographic Study of the Sodium Salt of iso-Hydroxytetrazole	i, 207
BÜLOW (CARL) and PETER NEBER. Action of Chlorine on Ethyl Phenyl-azooacetacetate. A New Way to Prepare Derivatives of Formimidochloride	i, 207
DAXIN (HENRY D.). The Racemisation of Proteins and their Derivatives Resulting from Tautomeric Change. I.	i, 208
ROBERTSON (T. BRAILSFORD). The Refractive Indices of Solutions of Certain Proteins. VIII. Globin	i, 209
ROBERTSON (T. BRAILSFORD). The Preparation and Properties of a Compound Protein; Globin Caseinate	i, 209
FISCHER (HANS) and ERICH BARTHOLOMÄUS. Constitution of the Blood and Bile Pigments. I.	i, 209
KÜSTER (WILLIAM) [and P. DRHLE]. Bilirubin and Hæmin	i, 210
AMBERG (SAMUEL) and WALTER JONES. The Action of Yeast on Yeast-nucleic Acid	i, 211
LEVENE (PHÉBUS A.) and F. B. LA FORGE. Nucleases. III.	i, 211
RINGER (WILHELM E.) and H. VAN TRIGT. Influence of the Reaction of the Medium on the Action of Ptyalin	i, 211
BOURQUELOT (ÉMILE) and MARC BRIDEL. Temperatures of Destruction of Emulsin in Ethyl Alcohol of Various Strengths	i, 212
ZIMMERMANN (A.). Rennin. Properties of the Ferment when Prepared by Different Methods. II. Acceleration of the Action of Rennin by Phosphoric Acid. III. The Variation in the Length of Time Required to Curdle Different Specimens of Milk	i, 212
KATZ (J. R.). Antagonism between Citrates and Calcium Salts in Milk Curdling by Rennet	i, 212
BOURQUELOT (ÉMILE) and HENRI HÉBISSEY. Synthesising Action between Galactose and Ethyl Alcohol under the Influence of Kephir	i, 213

Physiological Chemistry.

	PAGE
PORTER (E. L.). Variations in the Irritability of the Reflex Arc. I. Variations under Asphyxial Conditions with Blood-gas Estimations	i, 213
LONDON (EFIM S.) and N. A. DOBROVOLSKAJA. The Chemistry of Portal Blood. I. A Portal Fistula	i, 213
RONÁ (PETER) and F. ARNHEIM. Glycolysis. III.	i, 213
AUERBACH (FRIEDRICH) and HANS PICK. The Alkalinity of Pancreatic and Intestinal Juice in Living Dogs	i, 214
BAGLIONI (SILVESTRO) [with G. AMANTRA and L. MANINI]. Effects of Nutrition with Maize. IV. Action of the Succus entericus of the Dog on Zein, Gliadin, Zeoses, and Gliadoses	i, 214
MARÉŠ (FRANZ). Are the Endogenous Purine Substances the Products of the Activity of the Digestive Organs?	i, 214
SMETÁNKA (FRANZ). The Source of Uric Acid in Man. II.	i, 214
MCCRUDDEN (FRANCIS H.) and GRAHAM LUSK. Animal Calorimetry. VII. The Metabolism of a Dwarf	i, 215
ELIAS (HERBERT). The Part Played by Acid in Carbohydrate Metabolism Acid Diabetes	i, 215
EICHLÖV. Has Heated Milk the Same Feeding Value as Raw Milk?	i, 215
ARMSTRY (HENRY PRENTISS) and J. AUGUST FRIES. The Influence of Standing or Lying on the Metabolism of Cattle	i, 216
GRAFE (EDUARD) and K. TURBAN. Nitrogen Retention on Feeding with Urea	i, 216
STUDEL (HERMANN). Histochemistry of Spermatozoa. III.	i, 216
ROSENBLUM (JACOB). The Biochemistry of the Female Genitalia. I. The Lipins (Lipoids) of the Ovary and Corpus Luteum of the Pregnant and Non-Pregnant Cow	i, 216
LEVENE (PHÉBUS A.). The Sulphatide of the Brain	i, 216
HOLSTE (ARNOLD). The Influence of Quantity and Concentration of Poisons of the Digitalis Group on the Frog's Heart	i, 216
HOLSTE (ARNOLD). Systole and Diastole of the Heart Under the Influence of Digitalin	i, 216
BOMPIANI (R.). Replacement of Urea in Artificial Solutions for the Isolated Heart of Selachians	i, 217
EVANS (C. LOVATT). Toxicological Investigations on Bio-electric Currents. III. Comparative Toxicological Specificity of the Chemical Alteration Content, and Comparative Physiology and Toxicology of the Heart of <i>Helix pomatia</i>	i, 217
CARLSON (ANTON J.) and F. M. DRENNAN. Tolerance for Sugar in the Pig	i, 217
ITALLIE (LEOPOLD VAN) and J. J. VAN ECK. Occurrence of Metals in the Human Liver	i, 217
KASCHWARARA (M.). The Influence of Iodine on Autolysis	i, 218
POLLINI (LUIGI). The Catalytic Action of Iron Salts on the Autolysis of the Liver	i, 218
JUSCHTSCHENKO (A. S.). The Physiology of the Thyroid Glands. The Content of Phosphorus, Nitrogen, and Lipoids in the Organs of Thyroidectomised Animals	i, 218
SEIDELL (ATHERTON) and FREDERIC FENGER. Seasonal Variation in the Iodine Content of the Thyroid Gland	i, 219
BRADLEY (HAROLD C.). Enzyme Synthesis. IV. Lactase of the Mammary Gland	i, 219
BUGLIA (GIUSEPPE) and A. COSTANTINO. Muscle Chemistry. IV. The Extractive Nitrogen and the Free Amino-nitrogen, Titratable by Formaldehyde in the Musculature of Different Animals	i, 219
BUGLIA (GIUSEPPE) and A. COSTANTINO. Muscle Chemistry. V. Purine Bases of the Smooth Muscle of the Higher Animals	i, 219
SOROLÉV (NICOLAUS). The Formation of Lactic Acid in the Antiseptic Autolysis of Organs	i, 219

CONTENTS.

vii

	PAGE
BRADLEY (HAROLD C.) and E. KELLERBERGER. Enzyme Synthesis. II. Diastase and Glycogen of Animal Tissues	i, 219
BRADLEY (HAROLD C.). Enzyme Synthesis. I. Lipase and Fat of Animal Tissues	i, 220
VERNON (HORACE M.). The Influence of the Lipoids on the Action of Oxydases	i, 220
SCHULZ (ARTHUR). The Ferments of the Purine Group	i, 220
OKUDA (Y.). Creatine, Creatinine, and Monoamino-acids in Certain Fishes, Mollusca, and Crustacea	i, 221
STARKENSTEIN (EMIL) and MARTIN HENZE. The Occurrence of Glycogen in Sea-Molluscs (Especially <i>Cephalopods</i> and <i>Aplysiae</i>)	i, 221
REALE (ENRICO). Carbon Metabolism. The Labile and Stable Carbon of the Urine	i, 221
HENDERSON (LAWRENCE J.) and WALTER W. PALMER. The Intensity of Urinary Acidity in Normal and Pathological Conditions	i, 221
ELLIS (GEORGE W.) and JOHN A. GARDNER. The Origin and Destiny of Cholesterol in the Animal Organism. X. The Excretion of Cholesterol in Man when Fed on Various Diets	i, 222
LARRE (HENRI). Influence of Alkaline Salts in the Elimination of Urinary Ammonia by Normal Dogs	i, 222
SIGNORELLI (ERNESTO). The Relationship between the Nitrogen of the Amino-acids and Total Nitrogen in Urine under Various Normal and Pathological Conditions	i, 222
SAKAGUCHI (Kôzô). The Fat Content of Normal and Pathological Urine	i, 222
FROMHOLDT (G.) and N. NERESSEV. Urobilin. III. and IV.	i, 223
BRUGSCH (THEODOR) and KARL, RETZLAFF. Blood Destruction, Bile and Urobilin. The Formation of Bile Pigment in Blood. III.	i, 223
COOPER (EVELYN A.). The Protective and Curative Properties of Certain Foodstuffs against Polyneuritis Induced in Birds by a Diet of Polished Rice	i, 223
GARROD (ARCHIBALD E.) and W. H. HURLEY. Congenital Family Steatorrhœa	i, 224
GRÖS (OSKAR). The Mechanism of the Action of Silver Haloids	i, 224
KOLTZOV (N. K.). A Physiological Series of Cations	i, 224
BERTRAND (GABRIEL) and FLORENTIN MEDIGRECEANU. Temporary Fixation and Mode of Elimination of Manganese in the Rabbit	i, 224
ROTHFELD (J.). The Action of Certain Substances of the Chloroform Group on the Vestibular Eye-Reflex	i, 225
LEOTA (CAMILL LHOTÁK VON). The Fixation of Digitoxin (Merck) in the Organism of the Rabbit after Intravenous Injection. Comparative Experiments with Strophantigin	i, 225
DARIN (HENRY D.). The Fate of Proline in the Animal Body	i, 225
FRÖHLICH (ALFRED) and ERNST P. PICK. The Results of Poisoning with Adrenaline, Histamine, Pituitrin and Peptone in Relation to Anaphylaxis and the Vegetative Nervous System	i, 226
BICKEL (A.) and MICH. PAVLOV. The Pharmacological Action of <i>p</i> -Hydroxyphenylethylamine	i, 226
CUSHY (ARTHUR R.). Action of Scopolamine (Hyoscyne)	i, 226
MOLDOVAN (J.). The Method of Action of Quinine	i, 226
DESGREZ (ALEXANDRE) and DORLEANS. Influence of the Constitution of Purine Derivatives on their Action with Respect to Arterial Pressure	i, 227
SCHITTENHELM (ALFRED) and WOLFGANG WEICHARDT. The Biological Action of Certain Protein Products Introduced Parenterally	i, 227

Chemistry of Vegetable Physiology and Agriculture.

PENFOLD (W. J.) and (Mrs.) DOROTHY NORRIS. The Relation of Concentration of Food-supply to the Generation Time of Bacteria	i, 228
--	--------

	Page
CHICK (MISS HARRIETTE). The Bactericidal Properties of Blood Serum. I. The Reaction Velocity of the Germicidal Action of Normal Rabbit Serum on the <i>Bacillus coli commune</i> , and the Influence of Temperature Thereon	i, 228
THOMPSON (JAMES). Chemical Action of <i>Bacillus cloacae</i> (Jordan) on Citric and Malic Acids	i, 228
SASAKI (TAKAOKI). The Degradation of Polypeptides by Bacteria. II. The Action of the Non-liquefying Organisms	i, 228
SASAKI (TAKAOKI). The Degradation of Polypeptides by Bacteria. III. The Action of Liquefying Organisms	i, 229
WEHMER (CARL). Production of Citric Acid from Glycerol by Fungi	i, 229
WATERMAN (H. J.). Action of Hydrogen Ions, Boric Acid, Copper, Manganese, Zinc, and Rubidium on the Metabolism of <i>Aspergillus niger</i>	i, 229
BURROWSKI (J.). Influence of Zinc, Magnesium, Calcium, Potassium, and Sodium Salts on the Growth of <i>Aspergillus niger</i>	i, 230
KOSSOWICZ (ALEXANDER). Enzymatic Nature of Uric Acid and Hippuric Acid Fermentation	i, 230
POTTER (M. C.). The Rate of Fermentation as Measured by Difference of Potential	i, 230
NEUBERG (CARL) and J. KERB. Fermentations with Yeast in the Absence of Sugar. IX. Fermentation of Keto-acids by Wine Yeasts	i, 231
NEUBERG (CARL) and J. KERB. Fermentations with Yeast in the Absence of Sugar. X. The Fermentation of α -Ketobutyric Acid	i, 231
FERNBACH (AUGUST). The Acidification of Musts by Yeasts during Alcoholic Fermentation	i, 231
KOSSOWICZ (ALEXANDER). Fixation of Elementary Nitrogen by Yeasts, <i>Monilia candida</i> , and <i>Oidium lactis</i>	i, 231
MICHEELS (HENRI). Mode of Action of Dilute Solutions of Electrolytes on Germination	i, 231
RUSCHE (ALBERT). Effects of Manurial Salts on the Germination of Diff-rend Plants	i, 232
MAQUENNE (LÉON) and EM. DEMOUSSY. Influence of Previous Conditions on the Value of the Respiratory Quotient of Green Leaves	i, 232
ANDRÉ (GUSTAV). Hydrolysis and Displacement by Water by Nitrogenous and Mineral Substances Contained in Leaves	i, 233
STOKLASA (JULIUS) and E. SENFT. Does Potassium Participate in Building up and Degradation of Carbohydrates in Higher Plants?	i, 233
BRADLEY (HAROLD C.) and E. KELLERSBERGER. Enzyme Synthesis. III. Diastase and Starch of Plant Tissues	i, 233
JADIN (F.) and A. ASTRUC. Occurrence of Arsenic in the Vegetable Kingdom	i, 233
MONTMARTINI (L.). Stimulative Action of Manganese and Copper Sulphates on Plants	i, 234
WISSELINGH (C. VAN). Demonstration of Carotinoids in Plants. Separation in Crystalline Form	i, 234
WISSELINGH (C. VAN). Demonstration of Carotinoids in Plants. Behaviour of Carotinoids towards Reagents and Solvents	i, 234
WISSELINGH (C. VAN). Demonstration of Carotinoids in Plants. Leaf of <i>Urtica dioica</i> , the Flower of <i>Dendrobium thyrsiflorum</i> and <i>Haematooccus pluvialis</i>	i, 234
BYSSOLT (E.). Mannitol in the Sap of Asparagus	i, 235
TANKET (GEORGES). Presence of Stachyose in the Haricot and in the Seeds of Some Other Leguminosae	i, 235
MIMUROTO (Z.). Presence of Adenine and Aspartic Acid in Mulberry Leaves	i, 235
ROCAS (MANUEL). Action of Stimulants on Rice	i, 235
SUZUKI (UMETARA) and S. MATSUNAGA. Presence of Nicotinic Acid in Rice Bran	i, 235

CONTENTS

ix

	PAGE
JAVILLIER (MAURICE). The Substitution of Different Chemical Elements for Zinc in the Culture of <i>Sterigmatocystis nigra</i>	i, 235
DOX (ARTHUR W.) and RAY E. NEIDIG. Volatile Aliphatic Acids of Corn Silage	i, 236
ROSTWOROWSKI (S. GRAF). Action of Long-continued Exclusive Manuring on Plants and Soils	i, 236
BLANCK (EDWIN). Chemical and Physical Nature of "Roterden"	i, 236
HALL (ARCHIBALD A.). Analysis of a Florida Clay	i, 236
LYNDE (C. J.). Osmosis in Soils. Soils Act as Semipermeable Membranes. I.	i, 237
LYNDE (C. J.) and F. W. BATES. Osmosis in Soils. Soils Act as Semipermeable Membranes. II.	i, 237
FEIFFER (THEODOR) and EDWIN BLANCK. Importance of the Error of Analysis in Questions Relating to the Nitrogen Economy of Arable Soils	i, 238
MASCHHAUPT (J. G.) and L. R. SINNIGE. Estimation of the Value of Plant Foods in Soils and Manure so far as Dependent on Solubility	i, 238
LITMAN (CHARLES B.). Antagonism between Anions as Affecting Ammonification in Soils	i, 238
GERLACH (MAX) and ALFRED DENSCH. Influence of Organic Substances on the Decomposition and [Manurial] Action of Nitrogenous Compounds	i, 239
FRAPS (GEORGE S.). Relation of Active Potash to Pot Experiments	i, 239
FEIFFER (THEODOR) and EDWIN BLANCK. Effect of Sugar on the Fertility of Soils	i, 240
MILO (C. J.). Calcium Cyanamide	i, 240
HENSCHEL (G.). Behaviour of Calcium Cyanamide when Stored and under the Influence of Soil and Colloids	i, 240

PART II.

General and Physical Chemistry.

CRÖZE (F.). New Observations Relative to the Zeeman Effect in the Hydrogen Spectrum	ii, 85
ZAKRZEWSKI (CONSTANTIN). The Dispersion of Certain Metals in the Visible Spectrum	ii, 85
BERGER (F.) and JOHANNES KOENIGSBERGER. Electric Behaviour of Certain Vapours with Exhibit Absorption Bands	ii, 85
GANS (R.). The Absorption Curve of Colloidal Silver Solutions	ii, 85
GARRETT (CHARLES SCOTT). The Influence of Acid Radicles on the Colour Intensity of Copper Salts	ii, 85
JONES (HARRY C.) and J. SAM GUY. Absorption Spectra of Solutions as Affected by Temperature and by Dilution. Quantitative Study of Absorption Spectra by means of the Radiometer	ii, 86
BIELSKI (JEAN) and VICTOR HENRI. Quantitative Investigation of the Absorption of Ultra-violet Rays by the Fatty Acids and their Isomeric Esters	ii, 86
SCHUMM (OTTO). The Absorption Phenomena of Oxyhæmoglobin in the Grating Spectrum	ii, 86
GELBER (M.). Long- and Short-waved Absorption and Fluorescence Bands of the Carbonyl Group	ii, 87
DEUSSEN (ERNST). Rotation Dispersion	ii, 88
VOLZ (H.). The Rotation Dispersion of Some Coloured Lactates	ii, 88
FEER (PAUL C.) and HARRY D. GIBBS. Sunlight	ii, 88
BENNETT (CHARLES W.). Photochemical Reduction of Copper Sulphate	ii, 89

	PAGE
BERTHELOT (DANIEL) and HENRY GAUDECHON. The First Stages in the Photolysis of Ethyl Alcohol, Acetaldehyde, and Acetic Acid	ii, 90
BERTHELOT (DANIEL) and HENRY GAUDECHON. Photolysis of Different Complex Sugars (Bioses and Trioses) by Ultra-violet rays	ii, 90
BROCK (A. VAN DEN). The Radio-elements, the Periodic System, and the Constitution of the Atom	ii, 90
SVEDBERG (THEODOR). Evidence of Spontaneous Alterations of Concen- tration in Solutions and Gases	ii, 90
CHADWICK (JAMES). Excitation of γ -Rays by α -Rays	ii, 91
MARSDEN (E.) and H. RICHARDSON. Retardation of α -Particles by Metals	ii, 91
GRAY (J. A.). Absorption of β -Rays	ii, 92
GRAY (J. A.). Similarity in Nature of X- and Primary γ -Rays	ii, 92
WILSON (CHARLES T. R.). Expansion Apparatus for Making Visible the Paths of Ionising Particles in Gases, and the Results Obtained with this Apparatus	ii, 92
FLORANCE (D. C. H.). Ionisation Produced by β - and γ -Rays at High Pressures	ii, 92
PLIMPTON (S. J.). Recombination of Ions Produced by Röntgen Rays	ii, 94
TODD (GEORGE W.). Further Experiments on the Mobility of the Positive Ions at Low Pressures	ii, 94
THOMPSON (J. R.). Combination of Hydrogen and Oxygen in the Presence of Heated Platinum and Carbon	ii, 95
RUSSELL (ALEXANDER S.) and R. ROSSI. Investigation of the Spectrum of Ionium	ii, 95
KOHLRAUSCH (K. W. FRITZ). The Solid Radioactive Disintegration Pro- ducts Suspended in the Atmosphere	ii, 96
HERZFELD (KARL F.). Electro-chemistry of Extremely Dilute Solutions, in Particular of Radioactive Substances	ii, 96
CHRISTIANSEN (CHRISTIAN). Electrical Excitation in the Splashing of Liquids (Ballo-Electricity)	ii, 97
WALLEN (PAUL). Dielectric Constants of Dissolved Salts. II.	ii, 98
THOMÆ (CARL). Behaviour of Carbon on Electrical Pulverisation	ii, 99
BENEDICKS (CARL). Theory of the Electrical Synthesis of Colloids	ii, 99
DRUCKER (CARL), M. TABLE, and L. GOMEZ. The Mobility of the Bromide Ion in Water	ii, 99
PATERSON (J. HAMILTON). Investigation of the Chemical Reactions Taking Place at the Cathode and Anode During the Electrolysis of Simple Salt Solutions	ii, 100
PICCARD (AUGUSTE). The Constitution of Water and the Thermal Variation of its Magnetisation	ii, 100
FÄNDER (R.). New Thermo-regulator for Instantaneous Adjustment to any Given Temperature	ii, 100
DAY (ARTHUR L.) and ROBERT B. SOSMAN. The Expansion Coefficient of Graphite	ii, 101
WÜRSCHMIDT (J.). Volume Changes of Amalgams	ii, 101
PAGLIANI (STEFANO). Thermal Conductivity of the Metals and its Rela- tion to their Other Properties	ii, 101
BORN (MAX) and TH. VON KÄRMAN. Theory of Specific Heats	ii, 101
ESTREICHER (TADEUSZ) and M. STANIEWSKI. Specific Heat of Certain Elements at Low Temperatures	ii, 102
PIRANI (MARCELLO VON). Measurement of the Specific Heat of Solid Sub- stances at High Temperatures	ii, 102
MAGNUS (ALFRED). Measurements of Specific Heats of Solid Substances at High Temperatures	ii, 103
NERNST (WALTHER) and F. A. LINDEMANN. Investigations on Specific Heat. VI. Calculation of Atomic Heats	ii, 103
NERNST (WALTHER). Investigations on Specific Heat. VII. Calculation of Chemical Affinities	ii, 104
DUCLAUX (JACQUES). The Polymerisation of Substances at Low Tempe- ratures	ii, 104

CONTENTS.

xi

	PAGE
LEWIS (WILLIAM C. McC.). The Liquid Condition (Correction)	ii, 104
HAYAS (ERN.). Simple Method for Determining the Melting Point of the Less Fusible Substances	ii, 104
KANOLT (C. W.). Melting Point of Fire Bricks	ii, 105
PUSCHIN (NICOLAI A.) and I. V. GREEBENSCHIKOV. Pressure-temperature Diagrams for <i>p</i> -Azoxyanisole and α -Naphthylamine	ii, 105
LINDEN (T. VAN DER). Thermal Analysis	ii, 106
PASCAL (PAUL). Relations of Isomorphism in Organometallic Compounds.	
III. Derivatives of Bivalent Metalloids	ii, 107
LEWIS (WILLIAM C. McC.). Internal Pressure and Latent Heat of Liquids	ii, 107
LEDUC (ANATOLE). Guldberg's Law and the Corresponding States	ii, 108
VRYSKI (M. S.). Composition and Pressure of the Vapour of Solutions	ii, 108
DOLEZALEK (FRIEDRICH) and ALFRED SCHULZE. Association of Ethyl Ether and Chloroform in the Gaseous State	ii, 108
HAAKS (W. J. DE). Isotherms of Diatomic Gases and of their Binary Mixtures. XI. Determinations with the Volumenometer of the Compressibility of Gases under Small Pressures and at Low Temperatures	ii, 109
CARDOSO (ETTORE). The Critical Point	ii, 109
CARDOSO (ETTORE) and R. BELL. Critical Constants of Ethane, Carbon Dioxide, and Sulphur Dioxide	ii, 110
CARDOSO (ETTORE) and E. ARNI. Critical Constants of Ethylene, Nitrous Oxide, and Hydrogen Sulphide	ii, 111
CARDOSO (ETTORE) and (Mlle.) A. GILTAY. Critical Constants of Ammonia	ii, 111
CARDOSO (ETTORE) and A. F. O. GERMANN. Critical Constants of Hydrogen Chloride	ii, 111
LEWIS (GILBERT N.). Free Energy of Chemical Substances. Introduction	ii, 112
HANRIOT (MAURICE). Tempering [of Metals] without Deformation	ii, 112
MATHIAS (EMILE), H. KAMERLINGH ONNES, and C. A. CHOMMELIN. The Rectilinear Diameter for Argon	ii, 112
TSCHERNIAJ (N. A.). Specific Gravities of Saturated Aqueous Solutions of Various Salts at Different Temperatures	ii, 112
BAUME (GEORGES) and E. WOURTZEL. Compressibility of Gases	ii, 113
MAEO (ROBERT). Adsorption and Saturated Surfaces	ii, 113
KAROVSKI (ADAM V.). Adsorption. VII. Chemical Hysteresis of Starches	ii, 114
BROCHET (ANDRÉ). Relation between the Conductivity of Acids and their Absorption by Hide	ii, 114
FREUNDLICH (HERBERT) and A. N. SEAL. Some Properties of the Thiocyanate Ion	ii, 114
BOTTAZZI (FILIPPO) and E. D'AGOSTINO. Surface Tension of Protein Solutions. II.	ii, 115
TURNER (WILLIAM E. S.). Molecular Complexity in the Liquid State	ii, 115
MULLER (JOSEPH A.). Mode of Ionisation of Sulphuric Acid in Dilute Aqueous Solutions	ii, 115
SHORTER (SYDNEY A.). Application of the Theory of Chemical Potential to the Thermodynamical Theory of Solutions. III. Action of Gravity on a Solution. The Solute Potential. Extension of the Theory	ii, 115
WALKER (ERIC E.). Studies of the Processes Operative in Solutions. XX. The Conversion of Ammonium Cyanate into Carbamide, Especially as Influenced by Alcohols	ii, 116
WORLEY (FREDERICK P.). Studies of the Processes Operative in Solutions. XXI. Hydrolysis of Sucrose by Dilute Acids	ii, 117
WORLEY (FREDERICK P.). Studies of the Processes Operative in Solutions. XXII. Hydrolysis of Sucrose by Sulphuric Acid; Improvements in Polarimetric Apparatus	ii, 117
WORLEY (FREDERICK P.). Studies of the Processes Operative in Solutions. XXIII. Hydrolysis of Methyl Acetate by Acids	ii, 118
ARMSTRONG (HENRY E.) and FREDERICK P. WORLEY. Studies of the Processes Operative in Solutions. XXIV. Nature of the Hydrolytic Process	ii, 119

	PAGE
ROSENHAIN (WALTER) and DONALD EWEN. Inter-crystalline Cohesion in Metals and the Formation of Twinned Crystals in Silver	ii, 119
EDWARDS (CHARLES A.). Formation of Twin Crystals by Quenching and its Influence on the Hardness of Metals	ii, 120
HANNEMANN (H.). Etching at High Temperatures	ii, 120
BABY (PAUL). Colloids	ii, 120
BACHMANN (WILHELM). Determinations of the Volume of Voids in Silicic Acid Gels	ii, 121
BANCROFT (WILDER D.). Theory of Emulsification. IV.	ii, 121
HATSCHEK (EMIL). Composition of the Disperse Phase in Emulsoids	ii, 122
HATSCHEK (EMIL). The Existence and Probable Thickness of Adsorption Envelopes on Suspensoid Particles	ii, 122
BOISSOUDY (J. DE). The Equilibrium of a Gas in a State of Binary Dissociation	ii, 123
BRINER (EMIL) and E. L. DURAND. Action of Temperature on the Equilibrium of Nitrous and Nitric Acids Formed from the Oxides of Nitrogen and Water	ii, 123
VANDEVELDE (ALBERT J. J.). The Equilibrium in Acid Solutions of Potassium Salts. II.	ii, 123
SMITH (GEORGE MCPHAIL). Heterogeneous Equilibria between Aqueous and Metallic Solutions. II. Interaction of Mixed Salt Solutions and Liquid Amalgams	ii, 124
SOBYECOV (B.). Influence of Temperature on the Velocity of Chemical Reactions. I.	ii, 124
GRÖH (JULIUS). The Relation between Oxidation Potential and Oxidation Velocity	ii, 125
JOHANSSON (HJ.). Velocity of Reaction of Different Bases with Halogen-substituted Acids. II.	ii, 126
BOULANGER (CH.) and GEORGES URBAIN. Theory of Efflorescence. Influence of the Size of the Crystal	ii, 126
ORLOV (E. I.). Kinetics of Chemical Reactions of Combination, Deoxidation, and Oxidation. II.	ii, 127
ORLOV (E. I.). Kinetics of Chemical Reactions of Combination, Deoxidation, and Oxidation. III. and IV.	ii, 128
SACKUR (OTTO). Universal Significance of the Elementary Quantum	ii, 128
SACKUR (OTTO). The "Chemical Constants" of Di- and Tri-atomic Gases	ii, 128
SKALDT (M.). Volume and Valency	ii, 129
EPHRAIM (FRITZ). The Nature of Auxiliary Valencies. II. Metal Ammonias	ii, 129
EPHRAIM (FRITZ). The Nature of Auxiliary Valencies. III. The Region of the Existence of Auxiliary Valency Compounds	ii, 130
VORLÄNDER (DANIEL). What are Bases and Acids?	ii, 130
STEINKOPF (WILHELM) and HANS WINTERKUNTZ. New Shaking Apparatus	ii, 130
KEMPF (RICHARD). Shaking Apparatus, which can be Exhausted, Fitted with an Inner Temperature Regulator	ii, 131
TWISS (DOUGLAS F.). A Simple Experiment Illustrating the Luminosity of Phosphorus	ii, 131

Inorganic Chemistry.

CHATTAWAY (FREDERICK D.). Early Work on Hydrofluoric Acid and the Isolation of Fluorine	ii, 131
YAMACHI (YOSHITO). Reactions of Ozone with Certain Inorganic Salts	ii, 131
KRUYT (HUGO R.). The Dynamic Allotropy of Sulphur. IV.	ii, 132
FISCHER (FRANZ) and EMIL HENE. The Chemistry of the Formation of Nitric Oxide in the High Tension Arc	ii, 132
HILLER (FRITZ). The Inner Cone of Hydrocarbon Flames	ii, 133
FENNKE (CLARENCE N.). The Various Forms of Silica and their Mutual Relations	ii, 133

CONTENTS.

xiii

	PAGE
ENDELL (KURD) and REINHOLD RIEKE. The Transformations of Silica at High Temperatures	ii, 134
AMADORI (MARIO). Capacity of Potassium Haloids for Forming Solid Solutions at High Temperatures	ii, 134
OSWALD (MARCEL). Some Properties of Alkali Nitrites	ii, 135
CARPENTER (HENRY C. H.) and W. WHITELEY. The Silver-Zinc Equilibrium	ii, 135
CARPENTER (HENRY C. H.). The Copper-Zinc, Silver-Zinc, and Silver-Cadmium Equilibria	ii, 135
MADSEN (E. HÖST). The Preparation and Investigation of Silver Oxide	ii, 136
PARRAVANO (NICOLA). Cement Limestones of Santa Marinella	ii, 136
CAVAZZI. Gelatinous Calcium Sulphate and the Setting of Plaster	ii, 136
PROST (EUGÈNE) and MAURICE USAGHS. The Role of Calcium Sulphate and Barium Sulphate in the Reduction of Zinc Minerals	ii, 136
BLEYER (BENNO) and BR. MÜLLER. Glucinum Phosphates, and Glucinum Phosphite and Hypophosphite	ii, 137
HAUSER (OTTO). Magnesium Ions as Oxygen Carriers	ii, 137
SANDONINI (CARLO). Thermal Analysis of Binary Mixtures of Chlorides of Bivalent Elements. IV.	ii, 137
WOLFF (E. B.). [Metastable Metals]	ii, 138
COHEN (ERNST). [Metastable Metals]	ii, 138
MILBAUER (JAROSLAV). Physico-chemical Studies on Red Lead	ii, 138
CARPENTER (HENRY C. H.). The Structural Resolution of the Pure Copper-Zinc β -Constituent into $\alpha + \gamma$	ii, 138
CARPENTER (HENRY C. H.). The Effect of Other Metals on the Structure of the β -Constituent in Copper-Zinc Alloys	ii, 139
GUILLET (LÉON). Copper-Zinc-Nickel Alloys	ii, 139
MAHIN (EDWARD G.), D. C. INGRAHAM, and O. J. STEWART. Constitution of Aluminates	ii, 139
HEUSLER (FRIEDRICH). The Heusler Ferromagnetic Alloys of Manganese	ii, 139
ASZENASY (PAUL) and E. L. RENVY. The Formation of Nitrogen Oxides by Heating Manganese Dioxide in Air	ii, 139
MACLEOD-BROWN (JAMES). The Passive State of Iron	ii, 140
PARRAVANO (NICOLA). Equilibria in Quaternary Systems. VI. Quaternary Alloys of Iron, Nickel, Manganese, and Copper	ii, 140
GEHSNER DE CONINCK (WILLIAM). Determination of the Atomic Weight of Uranium	ii, 140
GEHSNER DE CONINCK (WILLIAM) and ALBERT RAYNAUD. The Oxides of Uranium	ii, 141
COPAU (HIPPOLYTE). The Basicity of the Tungsto-acids	ii, 141
SMITH (ANDREAS) and H. L. DE LEEUW. The System Tin	ii, 141
KLOOSTER (H. S. VAN). The System Tin-Iodine	ii, 142
HALLA (FRANZ). Thorium Compounds	ii, 142
FRANDT (WILHELM) and HERMANN MANZ. The Preparation of Metallic Vanadium. III.	ii, 142
EDGE (THOMAS K.). The Annealing of Coinage Alloys	ii, 143
WEIMANN (P. P. VON). Condition of Gold in Gold Quartz	ii, 143
HOLTZ (H. C.). Some Anomalies Observed in the Assay of Platinum Ores from Ural	ii, 143

Mineralogical Chemistry.

VERNADSKI (VLADIMIR I.). The Native Elements of the Earth's Crust	ii, 144
BAKUZIN (MICHAEL A.). Optical Investigation of Ural Naphtha	ii, 144
CAMPO (ANGEL DEL). White Sublimates of the Volcano Chinyero (Canaries)	ii, 145
CLARKE (FRANK W.). An Aluminium Arsenate from Utah	ii, 145
ROSTOKÉ (VOJTĚCH). Preslite [= Tsamebite], a New Mineral from Tsameb, German South-West Africa	ii, 145

	PAGE
PARRAVANO (NICOLA). Chemical Composition of the Haiyuite of the Albanian Hills	ii, 145
UHLIG (JOHANNES). Alunogen and Halotrichite	ii, 146
STROVICH (G.). Analysis of Garnet from Tavalato	ii, 148
WATSON (THOMAS L.). Kragerite, a Rutile-bearing Rock from Krageroe, Norway	ii, 148

Analytical Chemistry.

CARY-CURR (HENRY J.). Extraction Apparatus	ii, 146
FORBES (E. B.). Alundum not constant in Weight	ii, 147
KNOTT (J. M.) and W. R. WORKE. A Modification of the Frary Electro-dynamic Stirring Device	ii, 147
ARCHBUTT (LEONARD). Apparatus for Testing Water by Measurement of its Electrical Conductivity	ii, 147
GIRAL PEREIRA (JOSÉ). Colour Reactions of Hydrogen	ii, 147
GOOCH (FRANK A.) and PHILIP L. BLUMENTHAL. Use of Selenic Acid in the Estimation of Bromine Associated with Chlorine in Haloid Salts	ii, 148
BLUMENTHAL (PHILIP LEE). Preparation of Selenic Acid and Sodium Selenate Used in the Estimation of Bromine in Haloid Salts	ii, 148
TURNER (THOMAS). Oxygen in Brass	ii, 148
SPENCE (DAVID) and J. YOUNG. Comparison of Some Methods for the Estimation of Sulphur in Vulcanised Caoutchouc with Especial Reference to Electrolytic Oxidation	ii, 149
PELLET (HENRI). Estimation of Sulphurous Acid in Sugar Cane and Beet-root Products	ii, 149
DUYR (MAURICE). Estimation of Nitrites in Water	ii, 149
IVANOV (V. N.). Detection of Nitric Acid in Presence of Nitrous Acid	ii, 149
MASSINK (A.). Analysis of Mixtures of Nitric Acid, Carbamide, and Water	ii, 150
SCHLÖSSING, jun. (THEOPHILE). Detection and Estimation of Free White Phosphorus in Phosphorus Sesquisulphide	ii, 150
MÜLLER (EUGEN R. E.). Reduction of Manganese Dioxide by Nitrous Acid. Application of this Reaction in the Estimation of Phosphorus in Iron and Steel without Separation of Silicon	ii, 150
FRUNDLER (PAUL). The Estimation of Phosphorus in Lecithin	ii, 151
FAIRCHILD (JOHN G.). Accurate Volumetric Estimation of Phosphoric Acid in Phosphate Rock	ii, 151
KOHN-ABBEEST (EMILE). Use of "Activated" Aluminium in the Detection of Arsenic	ii, 151
ZUCCARI (GINO). Detection and Estimation of Arsenic in the Earth of a Cemetery	ii, 151
SCHÖRMANN (E.) and WILHELM BÖTTCHER. Estimation of Arsenic in Pyrites	ii, 152
BRES (F.). Phenolphthalein as a Double Indicator in the Estimation of Carbon in Castings, Steel, and Alloys by Direct Combustion	ii, 152
RICHTER (R.). Phenolphthalein as an Indicator of the Presence of Sodium Carbonate in Sodium Hydrogen Carbonate	ii, 152
BLACHER (CARL J.), P. GRÜNBERG, and M. KISSA. The Use of Potassium Palmate in Water Analysis	ii, 153
LORD Y GAMBOA (RAMÓN). Quantitative Separation of Calcium and Strontium	ii, 153
HORN VAN DEN BOS (J. L. M. VAN DER). Qualitative Separation of Barium, Strontium, and Calcium	ii, 153
VANNIER (L.). Estimation of Lead in Tin	ii, 153
PAZIENTI (UMBERTO). Use of Meyer's Reagent	ii, 154
LOYD (LORENZO L.) and WALTER M. GARDNER. A Case of Mercurial Poisoning, and the Estimation of Mercury in Textile Materials	ii, 154
LITTLE (HARRY F. V.). Estimation of Manganese by the Bismuthate Method	ii, 155

CONTENTS.

	PAGE
GORTNER (ROSS A.) and CLAYTON O. ROST. The Estimation of Total Manganese in Soils	ii, 155
GOTTFRIED (ARTHUR). Manganese and Phosphoric Acid Content of Honey	ii, 155
TASSILLY (EUGENE). Estimation of Iron in Waters	ii, 155
EASTICK (JOHN J.), JAMES P. OGILVIE, and JAMES H. LINDFIELD. Estimation of Traces of Iron in Cane and Beet Sugar Factory and Refinery Products	ii, 156
JAKUBOWSKI (S.). Rapid Estimation of Chromium in Chrome Mordants	ii, 156
ATACK (FREDERICK W.). Estimation of Stannous Chloride and of Chlorates by means of Methylene-blue	ii, 156
METZGER (FLOYD J.) and F. W. ZONS. A Volumetric Method for the Estimation of Thorium in the Presence of Other Rare Earths. The Analysis of Monazite Sand	ii, 157
FRANÇOIS (MAURICE). Analysis of Bismuth Subnitrate	ii, 157
LEVY (LEONARD A.). New Apparatus for the Examination of Mine Air	ii, 157
MCARTHY (ELLEN S.). The Estimation of Benzene in Coal Gas	ii, 158
LETTER (JOSEF). Estimation of Methyl Alcohol in Spirits	ii, 158
PENCK (C. M.). The Bromine and Iodometric Methods for the Volumetric Estimation of Crocol	ii, 158
ROLLY (FR.) and FR. OPPERMANN. The Behaviour of Blood-Sugar in Normal and Pathological Cases. I. The Technique of the Estimation of Sugar in Blood	ii, 159
FRIBOURG (C.). Analysis of Cane Molasses. Study of the Different Methods of Estimating Sucrose	ii, 159
PELLET (HENRI). Estimation of Sugar in "Bagasse" and in Sugar Cane. Estimation of Water in "Bagasse"	ii, 159
PELLET (HENRI). Polarimetric Estimation of Sugar in Beetroots, using the Cold and Hot Extraction Methods of Pellet	ii, 160
PELLET (HENRI). Determination of the Polarisation of Beetroot Sugar Products by Double Polarisation. Comparison between the Carbamide-Hydrochloric Acid and Sulphurous Acid Methods	ii, 160
NYMAN (MAX). The Gelatinising Temperature of Starch Grains	ii, 160
BERRY (HENRI) and (Mme.) Z. GATIN-GRUZEWSKA. New Method of New Method of Estimating Glycogen in the Liver	ii, 160
CROSS (CHARLES F.) and EDWARD J. BEVAN. The Estimation of Cellulose in Wood and Spinning Fibres	ii, 161
SHANNON (F. L.). Detection of Formic Acid in Fruit Products	ii, 161
NORMANN (WILHELM). Estimation of Acetyl Groups	ii, 161
KREIS (HANS) and EMIL ROTH. The Fractional Precipitation of Mixtures of Fatty Acids	ii, 161
MAIZEIN (PHILIPPE). Estimation of Total Tartaric Acid in Wines	ii, 161
GOWING-SCOPES (L.). Estimation of Citric Acid in the Presence of Certain Other Acids	ii, 162
RAALTE (A. VAN). Estimation of Salicylic Acid and Benzoic Acid in Fruit Juices, Jams, Lemonades, etc.	ii, 162
STEPHAN (ALFRED). Nuclein Metabolism	ii, 162
FOLIN (OTTO) and W. DENIS. A New Colorimetric Method for the Estimation of Uric Acid in the Blood	ii, 162
ALBERT. Comparison of the Hübl and Wysz Methods for Estimating the Iodine Numbers of Fats	ii, 163
RICHTER (OTTO). Relation between the Saponification, Iodine, and Refractometer Numbers of Fats and Oils	ii, 163
LEERS (HEINRICH). Detection of Earthnut Oil in Olive Oil by the Frauz-Adler Test	ii, 163
FOLIN (OTTO), W. B. CANNON, and W. DENIS. A New Colorimetric Method for the Determination of Epinephrine (Adrenaline)	ii, 163
INOUE (KATSUJI). Detection of Histidine	ii, 164
GRIMBERT (LEON) and M. LAUDET. Estimation of Lipoids in Blood-Serum	ii, 164
CHRISTIANSEN (JOHANN). Mett's Method for Estimating Pepsin and the Optimal Conditions of Peptic Activity	ii, 164

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS

A.

Ackermann, D., i, 181.
 Amadori, M., ii, 134.
 Amann, A. See J. Bradt.
 Amantea, G. See S. Baglioni.
 Amberg, S., and W. Jones, i, 211.
 André, G., i, 233.
 Angelico, F., and A. Coppola, i, 192.
 Archbutt, L., ii, 147.
 Armsby, H. P., and J. A. Fries,
 i, 216.
 Armstrong, H. E., and F. P. Worley,
 ii, 119.
 Arnheim, F. See P. Rona.
 Arni, E. See E. Cardoso.
 Askenasy, P., and E. L. Rényi,
 ii, 139.
 Astruc, A. See F. Jadin.
 Attack, F. W., ii, 156.
 Auerbach, F., and H. Pick, i, 214.
 August, ii, 163.
 Auld, S. J. M., and T. D. Moss crop,
 TRANS., 281.

B.

Bachmann, W., ii, 121.
 Baetcke, E. See H. Thoma.
 Baglioni, S., G. Amantea, and L.
 Manini, i, 214.
 Bancroft, W. D., ii, 121.
 Barbaschinov, N. See H. Stobbe.
 Bartholomäus, E. See H. Fischer.
 Bartsch, B. See J. von Braun.
 Bary, P., ii, 120.
 Baskerville, C., i, 155.
 Bates, F. W. See C. J. Lynde.
 Bauer, E. See A. Haller.
 Baume, G., and E. Woultzel, ii, 113.
 Beadle, C., and H. P. Stevens, i, 190.

Bell, J. M., and C. F. Cowell, i, 162.
 Bell, R. See E. Cardoso.
 Bellucci, L., i, 179.
 Benary, E., i, 191.
 Benedicks, C., ii, 99.
 Bennett, C. W., ii, 89.
 Benzinger, H. See E. Fromm.
 Berthelot, D., and H. Gaudechon,
 ii, 90.
 Bertrand, G., and F. Medigreceanu,
 i, 224.
 Bevan, E. J. See C. F. Cross.
 Bickel, A., and M. Pavlov, i, 226.
 Biddle, H. C., i, 179.
 Bielecki, J., and V. Henri, ii, 86.
 Bierry, H., and (Mmc.) Z. Catina-
 Gruzewska, ii, 160.
 Biltz, H., J. Kartle, and E. Topp,
 i, 166.
 Biron, E. von, i, 155.
 Bitterich, W. See E. Fromm.
 Blacher, C., P. Grünberg, and M.
 Kissa, ii, 153.
 Blanck, E., i, 236.
 Blanck, E. See also T. Pfeiffer.
 Bleicher, K., i, 156.
 Blendermann, K. See A. Kötz.
 Bleyer, B., and B. Müller, ii, 137.
 Blömer, A. See O. Piloty.
 Blumenthal, P. L., ii, 148.
 Blumenthal, P. L. See also F. A.
 Gooch.
 Böttcher, W. See E. Schürmann.
 Boissoudy, J. de, ii, 123.
 Bokhorst, S. C. See A. Smits.
 Bompiani, R., i, 217.
 Born, M., and T. von Kármán,
 ii, 101.
 Borsche, W., and J. Wollemann,
 i, 171.
 Bottazzi, F., and E. D'Agostino,
 ii, 115.
 Boulanger, C., and G. Urbain,
 ii, 126.

Bourquetot, E., and M. Bridel, i, 212.
 Bourquetot, E., and H. Hérissay, i, 213.
 Bousfield, W. R., *TRANS.*, 307.
 Bradley, H. C., i, 219, 220.
 Bradley, H. C., and E. Kellersberger, 219, 233.
 Braun, J. von, and B. Bartsch, i, 197.
 Braun, J. von, and A. Schmatloch, i, 196.
 Bredt, J., and A. Amann, i, 162.
 Bredt, J. P. Levy, and S. Link, i, 162.
 Brès, P., ii, 152.
 Bridel, M. See E. Bourquetot.
 Briner, E., and E. L. Durand, ii, 123.
 Brochet, A., ii, 114.
 Brock, A. vanden, ii, 90.
 Brugsch, T., and K. Retzlaff, i, 223.
 Bülow, C., and P. Neber, i, 207.
 Buglia, G., and A. Costantino, i, 219.
 Bunge, N. N., i, 160.
 Burger, F., and J. Koenigsberger, ii, 85.
 Buromski, J., i, 230.
 Busolt, E., i, 235.

C.

Campo, A. del, ii, 145.
 Cannon, W. B. See O. Folin.
 Cardoso, E., ii, 109.
 Cardoso, E., and E. Arni, ii, 111.
 Cardoso, E., and R. Bell, ii, 110.
 Cardoso, E., and A. F. O. Germann, ii, 111.
 Cardoso, E., and A. Giltay, ii, 111.
 Carlson, A. J. and F. M. Drennan, i, 217.
 Carpenter, H. C. H., ii, 135, 138, 139.
 Carpenter, H. C. H., and W. Whiteley, ii, 135.
 Carré, P., i, 156.
 Cary-Curr, H. J., ii, 146.
 Cavazzi, ii, 136.
 Chadwick, J., ii, 91.
 Chattaway, F. D., ii, 131.
 Chick, (Miss) H., i, 223.
 Christiansen, C., ii, 97.
 Christiansen, J., ii, 164.
 Clarke, F. W., ii, 146.
 Cohen, E., ii, 133.
 Cooper, E. A., i, 223.
 Coppaux, H., ii, 141.
 Coppola, A. See F. Angelico.

Costantino, A. See G. Buglia.
 Cowell, C. F. See J. M. Bell.
 Crommelin, C. A. See E. Mathias.
 Cross, C. F., and E. J. Bevan, ii, 161.
 Croze, F., ii, 86.
 Cushman, A. R., i, 226.
 Custodis, A. See A. Grün.

D.

Dakin, H. D., i, 203, 225.
 Day, A. L., and R. B. Sosman, ii, 101.
 D'Agostino. See F. Bottazzi.
 D'Alceo, O. G. See A. Mazzucchelli.
 Deihle, P. See W. Küster.
 Demoussy, E. See L. Maquenne.
 Denis, W. See O. Folin.
 Densch, A. See M. Gerlach.
 Desgrez, A., and Dorléans, i, 227.
 Deussen, E., ii, 88.
 Dobrochotow, W. See N. D. Zelin-ski.
 Dobrovol'skaja, N. A. See E. S. London.
 Dolezalek, F., and A. Schulze, ii, 108.
 Dorléans. See A. Desgrez.
 Dox, A. W., and R. E. Neidig, i, 236.
 Drennan, F. M. See A. J. Carlson.
 Drucker, C., L. Gomez, and M. Tarle, ii, 99.
 Duclaux, J., ii, 104.
 Durand, E. L. See E. Briner.
 Duyk, M., ii, 149.

E.

Eastick, J. J., J. P. Ogilvie, and J. H. Lindfield, ii, 156.
 Eck, J. J. van. See L. van Itallie.
 Edwards, C. A., ii, 120.
 Egorov, M. A., i, 165.
 Eichlov, i, 215.
 Elias, H., i, 215.
 Ellis, G. W., and J. A. Gardner, i, 222.
 Elsdon, G. D., i, 159.
 Endell, K., and R. Riecke, ii, 134.
 Engeland, R., and F. Kutscher, i, 194.
 Ephraim, F., ii, 129, 130.
 Estreicher, T., and M. Staniewski, ii, 102.
 Evans, C. L., i, 217.
 Evans, W. L., and L. H. Morgan, i, 173.
 Ewen, D. See W. Rosenhain.

F.

- Fänder, R., ii, 100.
 Fairchild, J. G., ii, 151.
 Fonger, F. See A. Seidell.
 Fenner, C. N., ii, 133.
 Fernbach, A., i, 231.
 Fischer, E., i, 177.
 Fischer, E., and H. Strauss, i, 180.
 Fischer, E., and K. Zach, i, 164.
 Fischer, F., and E. Hene, ii, 132.
 Fischer, H., and E. Bartholomäus, i, 209.
 Flaschen, J. See E. Fromm.
 Florance, D. C. H., ii, 93.
 Folin, O., W. B. Cannon, and W. Denis, ii, 163.
 Folin, O., and W. Denis, ii, 162.
 Forbes, E. B., ii, 147.
 Forster, A. See E. Fromm.
 Forster, M. O., and J. C. Withers, TRANS., 286.
 François, M., ii, 157.
 Fraps, G. S., i, 239.
 Freer, P. C., and H. D. Gibbs, ii, 89.
 Freundler, P., ii, 151.
 Freundlich, H., and A. N. Seal, ii, 114.
 Fribourg, C., ii, 159.
 Friedlaender, P., and S. Kielbasinski, i, 193.
 Fries, J. A. See H. P. Armsby.
 Fries, K., and H. Mengel, i, 163.
 Fröhlich, A., and E. P. Pick, i, 226.
 Fromholdt, G., and N. Nersessov, i, 223.
 Fromm, E., H. Benzinger and F. Schäfer, i, 174.
 Fromm, E., and W. Bitterlich, i, 204.
 Fromm, E., and J. Flaschen, i, 186.
 Fromm, E., A. Forster, and M. Klinger, i, 175.
 Fromm, E., A. Forster, and B. von Scherschewitzki, i, 176.
 Fromm, E., F. Haas, and E. Hubert, i, 184.
 Fromm, E., R. Heyder, A. Jung, and (Miss) M. Sturm, i, 204.

G.

- Gans, R., ii, 85.
 Gardner, J. A. See G. W. Ellis.
 Gardner, W. M. See L. L. Lloyd.
 Garrett, C. S., ii, 86.
 Garrett, C. S. See also J. C. Irvine.
 Garrod, A. E., and W. H. Hurtley, i, 224.
 Gattin-Gruzewska, (Mme.) Z. See H. Bierry.

- Gaudechon, H. See D. Berthelot.
 Gelbke, M., ii, 87.
 Gerlach, M., and A. Densch, i, 239.
 Germann, A. F. O. See E. Cardoso.
 Gibbs, H. D. See P. C. Freer.
 Giltay, A. See E. Cardoso.
 Giral Pereira, J., ii, 147.
 Godchot, M., and F. Taboury, i, 181, 182.
 Gomez, L. See C. Drucker.
 Gooch, F. A., and P. L. Blumenthal, ii, 148.
 Gortner, R. A., and C. O. Rost, ii, 155.
 Gottfried, A., ii, 155.
 Gowing-Scopes, L., ii, 162.
 Grafe, E., and K. Turban, i, 216.
 Gray, J. A., ii, 92.
 Grebenschtschikov, I. V. See N. A. Puschin.
 Grimbert, L., and M. Landet, ii, 184.
 Gröh, J., ii, 125.
 Gros, O., i, 224.
 Grün, A., and A. Custodia, i, 167.
 Grün, A., and F. Kade, i, 158.
 Grün, A., and B. Schreyer, i, 159.
 Grünberg, P. See C. Blacher.
 Guillet, L., ii, 139.
 Guy, J. S. See H. C. Jones.

H.

- Haas, F. See E. Fromm.
 Haas, W. J. de, ii, 109.
 Hale, W. J., and L. Thorp, i, 184.
 Hall, A. A., i, 236.
 Halla, F., ii, 142.
 Haller, A., and E. Bauer, i, 168.
 Hannemann, H., ii, 120.
 Hanriot, M., ii, 112.
 Hatschek, E., ii, 122.
 Hauser, O., ii, 137.
 Havas, E., ii, 104.
 Hendersson, L. J., and W. W. Palmer, i, 221.
 Hene, E. See F. Fischer.
 Henri, V. See J. Bielecki.
 Henschel, G., i, 240.
 Henze, M. See E. Starkenstein.
 Hérissey, H. See E. Bourquelot.
 Herzenstein, (Frl.) A. See N. D. Zelinski.
 Herzfeld, K. F., ii, 96.
 Hetper, J., ii, 168.
 Heusler, F., ii, 139.
 Heyder, R. See E. Fromm.
 Hiller, F., ii, 138.
 Hines, C. W. See A. F. Odell.
 Holde, D., i, 158.

Hollely, W. F. See R. Meldola.
 Holleman, A. F., and J. P. Wibaut,
 i, 169.
 Holste, A., i, 216.
 Holtz, H. C., ii, 143.
 Horn van den Bos, J. L. M. van der,
 ii, 153.
 Hubert, E. See E. Fromm.
 Hurtley, W. H. See A. E. Garrod.

I.

Ingraham, D. C. See E. G. Mahin.
 Inouye, K., ii, 164.
 Irvine, J. C., R. F. Thomson, and
 C. S. Garrett, TRANS., 238.
 Itallie, L. van, and J. J. van Eck,
 i, 217.
 Ivanov, V. N., ii, 149.

J.

Jackson, C. L., and W. N. Jones,
 i, 168.
 Jadin, F., and A. Astruc, i, 233.
 Jakubowski, S., ii, 156.
 Javillier, M., i, 235.
 Jegorov, J., i, 153.
 Johansson, H., ii, 126.
 Johnson, T. B., i, 203.
 Jones, H. C., and J. S. Guy, ii, 86.
 Jones, W. See S. Amberg.
 Jones, W. J., A. Lapworth, and
 H. M. Lingford, TRANS., 252.
 Jones, W. N. See C. L. Jackson.
 Jowett, H. A. D., and F. L. Pyman,
 TRANS., 290.
 Jung, A. See E. Fromm.
 Inuchtschenko, A. S., i, 218.

K.

Kade, F. See A. Grün.
 Kanolt, C. W., ii, 105.
 Kármán, T. von. See M. Born.
 Kastle, J. See H. Biltz.
 Kaschiwabara, M., i, 218.
 Katz, J. R., i, 212.
 Kellersberger, E. See H. C. Brad-
 ley.
 Kempf, R., ii, 131.
 Kenner, J., and E. Witham, TRANS.,
 232.
 Kerb, J. See C. Neuberg.
 Kettner, A. See A. Smits.
 Kielbasinski, S. See P. Fried-
 laender.

King, A. T. See W. H. Perkins.
 King, G., and H. McCombie, TRANS.,
 220.
 Kishner, N. M., i, 153, 187, 203.
 Kissa, M. See C. Blacher.
 Klinger, M. See E. Fromm.
 Klooster, H. S. van, ii, 142.
 Knote, J. M., and W. R. Worke,
 ii, 147.
 Koenigsberger, J. See F. Burger.
 Kötz, A., K. Blendermann, and
 J. Meyer, i, 179.
 Kohlrausch, K. W. F., ii, 96.
 Kohn-Abrest, E., ii, 151.
 Koltzov, N. K., i, 224.
 Kossowicz, A., i, 230, 231.
 Kreis, H., and E. Roth, ii, 161.
 Krossberg, W. See J. Tröger.
 Kruyt, H. R., ii, 132.
 Küster, W., and P. Deihle, i, 210.
 Kutscher, F. See R. Engeland.

L.

Labbé, H., i, 222.
 La Forge, F. B. See P. A. Levene.
 Lanfry, M., i, 193.
 Langheld, K., E. Meyer, and F. Opp-
 mann, i, 155.
 Lapworth, A. See W. J. Jones.
 Laudet, M. See L. Grimbart.
 Leduc, A., ii, 109.
 Leeuw, H. L. de See A. Smits.
 Leuchs, H., and G. Peirce, i, 194.
 Leuchs, H., and J. Wutke, i, 195.
 Levene, P. A., i, 216.
 Levene, P. A., and F. B. La Forge,
 i, 211.
 Levy, L. A., ii, 157.
 Levy, P. See J. Bredt.
 Lewis, G. N., ii, 112.
 Lewis, W. C. McC., ii, 104, 107.
 Lhota, C. L. von, i, 225.
 Lindemann, F. A. See W. Nernst.
 Linden, T. van der, ii, 106.
 Lindfield, J. H. See J. J. Eastick.
 Lingford, H. M. See W. J. Jones.
 Link, S. See J. Bredt.
 Lippman, C. B., 238.
 Lippmann, E. O. von, i, 155.
 Little, H. F. V., ii, 155.
 Littleton, L. R. See W. A. Noyes.
 Llord y Gamboa, R., ii, 153.
 Lloyd, L. L., and W. M. Gardner,
 ii, 154.
 London, E. S., and N. A. Dobrovols-
 kaja, i, 213.
 Lüers, H., ii, 163.
 Lusk, G. See F. H. McCrudden.

Lynde, C. J., i, 237.
Lynde, C. J., and F. W. Bates, i, 237.

M.

McCarthy, E. S., ii, 158.
McCombie, H. See G. King.
McCrudden, F. H., and G. Lusk, i, 215.
MacLeod-Brown, J., ii, 140.
Madinaveitia, A., and J. Sureda Blanes, i, 177.
Madsen, E. H., ii, 136.
Magnus, A., ii, 103.
Mahin, E. H., D. C. Ingraham, and O. J. Stewart, ii, 139.
Mailhe, A., i, 173.
Maillard, L. C., i, 185.
Malvezin, P., ii, 161.
Manini, L. See S. Baglioni.
Manz, H. See W. Prandtl.
Maquenne, L., and E. Demoussy, i, 232.
Marc, R., ii, 113.
Mareš, F., i, 214.
Marsden, E., and H. Richardson, ii, 91.
Mascarelli, L., i, 171.
Maschhaupt, J. G., and L. R. Sinuige, i, 238.
Massink, A., ii, 150.
Mathias, E., C. A. Crommelin, and H. K. Onnes, ii, 112.
Matsunaga, S. See U. Suzuki.
Mazzucchelli, A., and O. G. D'Alceo, i, 160.
Medigreceanu, F. See G. Bertrand.
Meldola, K., and W. F. Holley, TRANS., 177.
Mengel, H. See K. Fries.
Merton, T. R., TRANS., 249.
Metzger, F. J., and F. W. Zons, ii, 157.
Meyer, E. See K. Langheld.
Meyer, H., and K. Steiner, i, 204.
Meyer, J. See A. Kütz.
Michaelis, L., and P. Rona, i, 164.
Michels, H., i, 231.
Milbauer, J., ii, 138.
Milo, C. J., i, 240.
Mimuroto, Z., i, 235.
Mohr, E., i, 155.
Moldovan, J., i, 226.
Montemartini, i, 234.
Morgan, L. H. See W. L. Evans.
Moscrop, T. D. See S. J. M. Auld.
Müller, B. See B. Bleyer.
Müller, E. R. E., ii, 150.
Muller, J. A., ii, 115.
Mylo, B. See A. Wohl.

N.

Neber, P. See C. Bülow.
Neidig, E. E. See A. W. Dox.
Nelson, E. K., i, 189.
Nernst, W., ii, 104.
Nernst, W., and F. A. Lindemann, ii, 103.
Nersesov, N. See G. Fromholdt.
Neuberg, C., and J. Kerp, i, 231.
Nierenstein, M., and F. W. Rixon, i, 180.
Normann, W., ii, 161.
Norris, (Mrs.) D. See W. J. Penfold.
Noyes, W. A., and L. R. Littleton, i, 161.
Nyman, M., ii, 160.

O.

Odell, A. F., and C. W. Hines, i, 172.
Oechsner de Coninck, W., ii, 140.
Oechsner de Coninck, W., and A. Raynaud, ii, 141.
Ogilvie, J. P. See J. J. Eastick.
Okuda, Y., i, 221.
Onnes, H. K. See E. Mathias.
Oppermann, F. See F. Rolly.
Oppmann, F. See K. Langheld.
Orlov, E. I., ii, 127, 128.
Oswald, M., ii, 135.

P.

Padoa, M., and G. Rotondi, i, 188.
Pagliani, S., ii, 101.
Palmer, W. W. See L. J. Henderson.
Parravano, N., ii, 138, 140, 145.
Pascal, P., ii, 107.
Paterson, J. H., ii, 100.
Patterson, T. S., TRANS., 145.
Pavlov, M. See A. Bickel.
Pazienti, U., ii, 154.
Peachey, S. J., i, 190.
Peirce, G. See H. Leucha.
Pellet, H., ii, 149, 159, 160.
Pence, C. M., ii, 158.
Penfold, W. J., and (Mrs.) D. Norris, i, 223.
Perkin, A. G., TRANS., 209.
Perkins, W. H., and A. T. King, TRANS., 300.
Pfeiffer, T., and E. Blanck, i, 238, 240.
Philip, J. C., TRANS., 284.

Piccard, A., ii, 190.
 Pick, E. P. See A. Fröhlich.
 Pick, H. See F. Auerbach.
 Piloty, O., and A. Blömer, i, 196.
 Pirani, M. von, ii, 102.
 Plimpton, S. J., ii, 94.
 Pollini, L., i, 218.
 Porter, E. L., i, 218.
 Potter, M. C., i, 230.
 Power, F. B., and A. H. Salway,
 TRANS., 191.
 Prandtl, W., and H. Manz, ii, 142.
 Prost, E., and M. Ubaghs, ii, 136.
 Raschin, N. A., and I. V. Greben-
 schtschikov, ii, 105.
 Pyman, F. L. See H. A. D. Jowett.

R.

Raalte, A. van, ii, 162.
 Rakovski, A. V., ii, 114.
 Rakuzin, M. A., ii, 144.
 Ramsay, Sir W., TRANS., 264.
 Raynaud, A. See W. Gschäner de
 Gouinck.
 Reale, E., i, 221.
 Rechenberg, W. von. See O. Wal-
 lach.
 Rényi, E. L. See P. Askenasy.
 Retzlaff, K. See T. Brugsch.
 Richardson, H. See E. Marsden.
 Richter, O., ii, 163.
 Richter, R., ii, 152.
 Riecke, R. See K. Endell.
 Ringer, W. E., and H. van Trigt,
 i, 211.
 Risse, F. See F. W. Semmler.
 Rixon, F. W. See M. Nierenstein.
 Robertson, T. B., i, 209.
 Robson, S., i, 177.
 Roess, M., i, 235.
 Roeh, H. See E. von Walther.
 Rolly, P., and F. Oppermann,
 ii, 159.
 Rola, P., and F. Arnheim, i, 218.
 Rons, P. See also L. Michaelis.
 Rosati, A., i, 207.
 Rose, T. K., ii, 143.
 Rosenbloom, J., i, 216.
 Rosenbain, W., and D. Ewen, ii, 119.
 Rossický, V., ii, 145.
 Rossi, R. See A. S. Russell.
 Rost, C. O. See R. A. Gortner.
 Rostworowski, S. G., i, 236.
 Roth, E. See H. Kreis.
 Rothfeld, J., i, 225.
 Rotondi, G. See M. Padoa.
 Rusche, A., i, 232.
 Russell, A. S., and R. Rossi, ii, 95.

S.

Sackur, O., ii, 128.
 Sakaguchi, K., i, 222.
 Salway, A. H. See F. B. Power.
 Sandonini, C., ii, 137.
 Sasaki, T., i, 228, 229.
 Scagliarini, G., i, 166.
 Schäfer, F. See E. Fromm.
 Scherschewitzki, B. von. See E.
 Fromm.
 Schittenhelm, A., and W. Weich-
 ardt, i, 227.
 Schloesing, T., jun., ii, 150.
 Schmatloch, A. See J. von Braun.
 Schöttle, J., i, 197.
 Schreyer, B. See A. Grün.
 Schürmann, E., and W. Rottcher,
 ii, 152.
 Schulz, A., i, 220.
 Schulze, A. See F. Dolezalek.
 Schumm, O., ii, 87.
 Schvecov, B., ii, 124.
 Seal, A. N. See H. Freundlich.
 Sebaldt, M., ii, 129.
 Seidell, A., and F. Fenger, i, 219.
 Semmler, F. W., and F. Risse, i, 188.
 Senft, E. See J. Stoklassa.
 Shannon, F. L., ii, 161.
 Shorter, S. A., ii, 115.
 Signorelli, E., i, 222.
 Sinnige, L. R. See J. G. Masch-
 haupt.
 Sirovich, G., ii, 146.
 Smetánka, F., i, 214.
 Smith, G. McP., ii, 124.
 Smits, A., and S. C. Bokhorst,
 i, 187.
 Smits, A., and A. Kettner, i, 167.
 Smits, A., and H. L. de Leeuw,
 ii, 141.
 Smythe, J. A., i, 174.
 Sobolev, N., i, 219.
 Soaman, R. B. See A. L. Day.
 Spence, D., and C. A. Ward, i, 191.
 Spence, D., and J. Young, ii, 149.
 Staniewski, M. See T. Estreicher.
 Starkenstein, E., and M. Henze,
 i, 221.
 Steiner, K. See H. Meyer.
 Steinkopf, W., and H. Winternitz,
 ii, 130.
 Stephan, A., ii, 162.
 Stephan, H., and C. Weizmann,
 TRANS., 269.
 Steudel, H., i, 216.
 Stevens, H. P. See C. Beadle.
 Stewart, O. J. See E. G. Mahin.
 Stobbe, H., and N. Barbaschinov,
 i, 177.
 Stoklassa, J., and E. Senft, ii, 233.

Strauss, H. See E. Fischer.
 Sturm, (Miss) M. See E. Fromm.
 Sureda Blanes, J. See A. Madina
 veitia.
 Suzuki, U., and S. Matsunaga,
 i, 235.
 Svedberg, T., ii, 90.

T.

Taboury, F. See M. Godchot.
 Tanret, G., i, 235.
 Tarbouriech, P. J., i, 131.
 Tarle, M. See C. Drucker.
 Tassilly, E., ii, 165.
 Thomae, C., ii, 99.
 Thompson, J., i, 228.
 Thompson, J. R., ii, 95.
 Thoms, H., and E. Baetcke, i, 192.
 Thomson, R. F. See J. C. Irvine.
 Thorp, L. See W. J. Hale.
 Thorpe, J. F., and A. S. Wood,
 TRANS., 276.
 Todd, G. W., ii, 94.
 Topp, E. See H. Biltz.
 Trigt, H. van. See W. E. Ringer.
 Trobridge, F. G., i, 160.
 Trüger, J., and W. Kroseberg, i, 169.
 Tschernaj, N. A., ii, 112.
 Turban, K. See E. Grafe.
 Turner, T., ii, 148.
 Turner, W. E. S., ii, 115.
 Twiss, D. F., ii, 131.

U.

Ubaghs, M. See E. Prost.
 Uhlig, J., ii, 145.
 Uklonskaja, N. See N. D. Zelinski.
 Urbain, G. See C. Boulanger.

V.

Vandavelde, A. J. J., ii, 123.
 Vannier, L., ii, 153.
 Vernadski, V. L., ii, 144.
 Vernon, H. M., i, 220.
 Vignon, L., i, 153.
 Volk, H., ii, 88.
 Vorländer, D., ii, 130.
 Vrevski, M. S., ii, 108.

W

Walden, P., ii, 98.
 Walker, E. E., ii, 116.
 Wallach, O., and W. von Rechen-
 berg, i, 182.
 Walther, R. von, and H. Roch,
 i, 193.
 Ward, C. A. See D. Spence.
 Waterman, H. J., i, 229.
 Watson, T. L., ii, 146.
 Wehmer, C., i, 229.
 Weichardt, W. See A. Schitten-
 helm.
 Weimaru, P. P. von, ii, 149.
 Weizmann, C. See H. Stephan.
 Whiteley, W. See H. C. H. Carpenter.
 Wibaut, J. P. See A. F. Holleman.
 Wilson, C. T. R., ii, 92.
 Winternitz, H. See W. Steinkopf.
 Wisselingh, C. van, i, 234.
 Witham, E. See J. Kenner.
 Withers, J. C. See M. O. Forster.
 Wohl, A., and B. Mylo, i, 163.
 Wolff, E. B., ii, 138.
 Wollemann, J. See W. Borsche.
 Wood, A. S. See J. F. Thorpe.
 Worke, W. R. See J. M. Knot.
 Worley, F. P., ii, 117, 118.
 Worley, F. P. See H. E. Armstrong.
 Wourtzell, E. See G. Baume.
 Würschmidt, J., ii, 101.
 Wutke, J. See H. Leuchs.

Y.

Yabuta, T., i, 180.
 Yamauchi, P., ii, 131.
 Young, J. See D. Spence.

Z.

Zach, K. See E. Fischer.
 Zakrzewski, C., ii, 85.
 Zelinski, N. D., W. Dobrochotow,
 and (Frl.) A. Herzenstein, i, 167.
 Zelinski, N. D., and N. Uklonskaja,
 i, 176.
 Zimmermann, A., i, 212.
 Zons, F. W. See F. J. Metzger.
 Zuccàri, G., ii, 151.

ERRATA.

xxiii

ERRATA.

VOL. CII (ABSTR., 1912).

Page.	Line.	
ii, 1182	12*	for "birefraction" read "birefringence."

VOL. CIV (ABSTR., 1913).

i, 84	1	for " <i>Pilocarpus</i> " read " <i>Pilocarpus</i> ."
	3	for "pilocarpiline" read "carpilene."
191	8	"SPENCER" read "SPENCE."
ii, 68	16*	"Sardaigne" read "Sardinia."
	16*	"CESARO" read "CESÀRO."
	13* 9*	"orthose" ,, "orthoclase."

* From bottom.

XXI.—*An Attempt to Harmonise, Qualitatively, the Relation between Temperature and Rotation for Light of all Refrangibilities of Certain Active Substances, both in the Homogeneous State and in Solution.*

By THOMAS STEWART PATTERSON.

It would probably be fairly generally conceded that the work of the past hundred years on optical activity, instead of reducing has tended to increase the difficulty of the subject, and to render it, as time goes on, less, rather than more, capable of generalisation, because of the great diversity of the causes the effects of which have first to be discovered and then brought into relationship. It has become clear, of course, that optical rotation, which depends, in the first place, on the chemical nature of the active substance, depends also on the temperature and on the wave-length of the light used. Considering the large number of active compounds now known, the generalisation of this field alone constitutes an immense problem, but if the active substance be mixed with an indifferent medium, there must further be taken into account the nature of the solvent and the concentration, whilst the temperature and colour of light must be considered afresh, since their influence may be entirely different in the new circumstances from what obtained for the homogeneous compound.

The number of variables is thus large, and the chief reason why no really comprehensive scheme has been possible is that the connexion between the rotation and these other variables has seldom been studied in a thoroughly systematic manner.

In regard to one of these variables, and that, perhaps, the most important, the course of events was distinctly unfortunate, for although Biot showed, in some of his later papers, that the rotation of an active compound is not independent of temperature, the importance of this factor, on account of his earlier work, was greatly underrated by subsequent investigators, with the result that much of the experimental material they accumulated is practically useless for purposes of generalisation. In the last twenty years, however, and chiefly owing to the example of P. F. Frankland, the examination of an active compound over as wide a range of temperature as possible is gradually becoming, as it ought to be, a matter of ordinary routine.

The discovery of the first example of what seems likely to prove an important phenomenon in this connexion was made by Frankland and Wharton (T., 1896, 69, 1587) some sixteen years ago,

when they found that ethyl dibenzoyltartrate in the homogeneous condition shows a distinct maximum negative rotation at a temperature of 60° , whilst in a previous paper (T., 1896, **69**, 1309) these authors give data which strongly indicate the existence of maximum negative rotations, at temperatures of about 20° , for methyl *o*-toluoyl-, ethyl *o*-toluoyl-, and ethyl *m*-toluoyl-tartrates. Some years afterwards Grossmann and Pötter (*Ber.*, 1904, **37**, 84) found that ammonium and sodium molybdanyldimalates, at several concentrations, show maximum rotations* at 35° and 50° respectively, and about the same time Patterson (T., 1904, **85**, 1116) found maxima in the temperature-rotation curves for solutions of sodium and potassium tartrates, of potassium methyl, potassium ethyl, and potassium *n*-propyl tartrates, and probably also in solution of methyl and ethyl tartrates. Then Patterson and Taylor (T., 1905, **87**, 33) discovered an instance strictly analogous to the ethyl dibenzoyltartrate of Frankland and Wharton while examining menthol, which was found to have a maximum negative rotation of -77 - 94° between 58° and 59° . Some years previously Winther (*Zeitsch. physikal. Chem.*, 1902, **41**, 176), assuming that the relationship between rotation and temperature of ethyl tartrate may be represented by a parabolic equation, deduced from his results for this ester—as well as for methyl tartrate and propyl tartrate—a maximum specific rotation at a temperature of 149° , and Patterson, a few years afterwards (T., 1908, **93**, 1843), showed that a maximum does exist, but at a temperature of 175° , and, further, that when the ester is dissolved in nitrobenzene and a number of other similar solvents, the maximum persists, and is observed to move towards a higher value and a lower temperature with increasing dilution. Later Patterson and McDonald (T., 1909, **95**, 323) found that a $p=10$ solution of ethyl tartrate in quinoline has a minimum rotation of 16° at a temperature of about 94° . Again, Patterson and Miss Stevenson (T., 1910, **97**, 2121) pointed out the existence of maxima in resorcinol-, quinol-, *m*-nitrophenol-, etc., solutions of ethyl tartrate; Pickard and Kenyon (T., 1911, **99**, 52, footnote) record the occurrence of minimum rotations for methyl-*n*-butyl- and methyl-*n*-octyl-carbinols at about 125° and in six other alcohols (T., 1912, **101**, 626); Cohen (T., 1911, **99**, 1060) discovered a maximum negative rotation for menthyl-*o*-iodobenzoate at about 60° , whilst Patterson and Davidson (T., 1912, **101**, 374) observed that ethyl, isobutyl, and probably also methyl, di-trichloroacetyl-tartrates show minima in their temperature-rotation curves, and that these minima persist in solution in nitrobenzene and move with increasing dilution towards a lower temperature and a lower value.

Thus a number of homogeneous substances and some of them also in solution present the phenomenon of a maximum or minimum rotation at a definite temperature, and, if the importance of singular points in the mathematical treatment of curves is remembered, it would seem probable that such singular points as those mentioned will ultimately prove to be of the greatest value in regard to the theory of optical activity. For the great difficulty which has always been found in discussing the influence of temperature on rotation is that no criterion exists meanwhile to justify a decision as to which parts of two curves represent the optical properties of the compounds in really comparable conditions. The great merit therefore of a point of maximum rotation is its recognisability; for, if it be assumed that a point of maximum rotation indicates that condition of a substance in which one of the groups attached to the asymmetric atom attains to a maximum influence, then a maximum rotation for another closely related substance may legitimately be taken to represent its optical properties in, at the very least, a similar condition.

The Rotation of Homogeneous Compounds.

From this point of view further information in regard to maximum rotations such as described above seemed desirable, the immediate objects of the present investigation being, firstly, to ascertain whether the rotations of other simple esters of tartaric acid also reach maximum values, and, secondly, how these maxima, if they exist, are related to each other. In order to test these points the ethyl,* *n*-propyl, *sec*-propyl, allyl, *isobutyl*, *isoamyl*, *sec*-octyl, and benzyl esters of tartaric acid, of which the fourth and the last appear to be new, have been examined, as regards rotation, over a considerable range of temperature. The experimental data are recorded at the end of the paper, where also some points arising out of these data, but not directly concerned with the main purpose of the investigation, are referred to.

Fig. 1 reproduces the curves for the molecular rotation of these esters, and, on the whole, the graphs are obviously alike in general characteristics,† but it will be clear that, even for such closely similar substances as these, the institution of comparisons between the rotation values at any one given temperature could hardly be expected to yield satisfactory results. The data for the esters at 20° would not be in the same sequence as at, say, a temperature

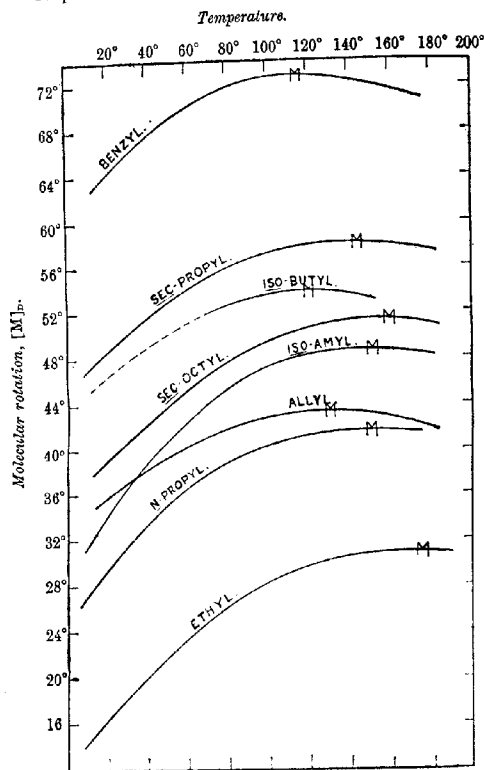
* The maximum rotation of methyl tartrate occurs at a temperature a little too high to be estimated by the apparatus at the disposal of the author.

† It should be noted that the maximum in observed rotation occurs at a lower temperature than the maximum for molecular rotation.

of 180°. At the former temperature, allyl tartrate has a higher rotation than has *iso*amyl tartrate, whereas at the latter the reverse is the case, and other similar examples will be obvious from the figure.

FIG. 1.

Temperature-rotation curves for various esters of tartaric acid.



As regards the values of the maximum rotations, it will be clear, in the first place, that they do not all occur at the same temperature. The actual details will be found in the following table. All that need be said in the meantime regarding these data is that, roughly, the value of the maximum molecular rotation is higher the lower the temperature at which it occurs.

TABLE I.

Maximum Rotation Values and the Temperatures at which they occur for Certain Esters of Tartaric Acid.

Ester.	Maximum α_D .	T .	Maximum $[\alpha]_D$.	T .*	Maximum $[M]_D$.
Diethyl tartrate..	+15.93°	148.0°	+15.0°	175°	30.9°
Di-n-propyl tartrate	18.3	115.0	17.8	150	41.65
Di-sec.-propyl "	25.2	93.0	24.8	144	58.03
Di-isobutyl "	20.65	93.0	20.57	120	53.9
Di-isomyl "	16.1	118.5	16.8	151	48.72
Di-sec.-octyl "	12.4	122.5	13.76	160	51.46
Diallyl "	20.75	100.0	18.8	130	43.24
Dibenzyl "	26.1	88.0	22.06	115	72.80

It has already been remarked that the effect of temperature on rotation is thus very difficult to trace; for example, it has often been found that two compounds intimately related chemically show an exactly opposite behaviour as regards the influence of temperature change on their rotations. A considerable number of examples of this behaviour could be cited, but one will probably suffice. The rotation of ethyl diacetyltartrate (McCrae and Patterson, T., 1900, **77**, 1106) increases with rise of temperature; that of ethyl di-monochloroacetyltartrate increases by about the same amount, whilst that of ethyl di-dichloroacetyltartrate is almost unchanged by alteration of temperature from 15° to 100° (Frankland and Patterson, T., 1896, **73**, 207), but that of ethyl diphenacetyltartrate diminishes rapidly as the temperature rises. There is obviously, underlying this behaviour, a distinct regularity, but it is one which cannot readily be expressed in a general manner.

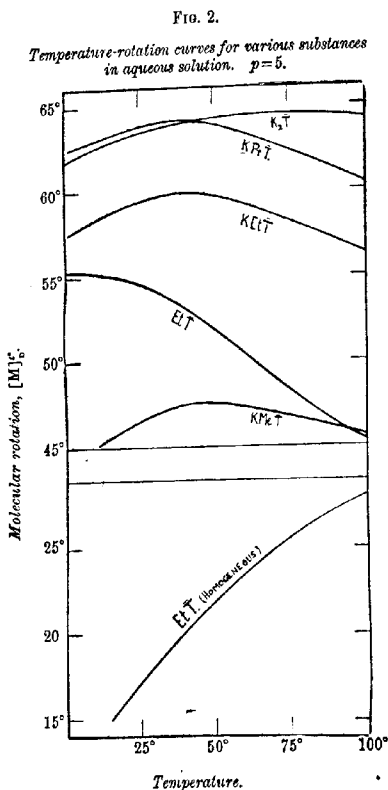
In considering the very similar case of the dialkyltartrates, the potassium alkyltartrates, and dipotassium tartrate (Fig. 2), all in dilute aqueous solution, the author suggested that the rotation-temperature curves represented, "in the case of the dialkyltartrate, only one limb, the descending one; for the potassium alkyltartrates, both limbs, and for potassium and sodium tartrates, again only one limb, the ascending one, of curves which are in all three cases of a similar kind" (T., 1904, **85**, 1142). In other words, the temperature-rotation curves of chemically similar substances are of the same type, but the maximum does not occur in each at the same temperature. For one compound it may lie towards a low temperature outside the range of the experiments, in which case the temperature-coefficient of the rotation will be negative, that is, the rotation will decrease as the temperature rises. For

* The maxima for specific, and molecular, rotation occur, of course, at the same temperatures.

another compound the maximum may lie towards a high temperature outside the range of the experiments, when, of course, the temperature-coefficient at the ordinary temperature will be positive, the rotation will increase with rise of temperature.

For the homologous alkyl esters of tartaric acid, the curves of

which are represented in Fig. 1, the temperature of maximum rotation does not vary much; for compounds related to each other, as are diethyl tartrate, ethyl potassium tartrate, and dipotassium tartrate, the difference is much greater. The temperature of maximum molecular rotation for diethyl tartrate lies at 175° ; for homogeneous potassium ethyl tartrate it would lie in the neighbourhood of 70° (T., 1904, 85, 1123, Fig. 5), and for dipotassium tartrate at a much lower temperature, which cannot even be roughly estimated (*ibid.*, p. 1119, Fig. 2). The conception, therefore, of the existence of a maximum rotation outside the tempera-



ture range of the experiments is sufficient at once to account for the occurrence, within the ordinary range of temperature, of opposite temperature-coefficients for analogous compounds.

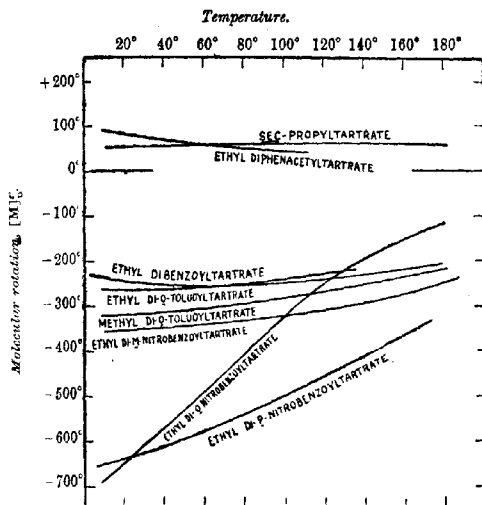
Now, as has already been mentioned, the prediction of maxima is a necessary consequence of the assumption that the temperature-rotation curve of an active compound is of parabolic form, but

since the parabola is a symmetrical curve, it would also follow that the two limbs of the temperature-rotation curve should be identical in shape,* and that the rotation should diminish constantly on both sides of the maximum value. It is of some interest, therefore, to ascertain, if possible, whether these are really parabolas.

Unfortunately the range of temperature over which rotation can be examined is usually comparatively short; at high temperatures there is the possibility of decomposition of the substance or the difficulty of finding a suitable tube to contain it, and at low

FIG. 3.

Temperature rotation curves for various esters.



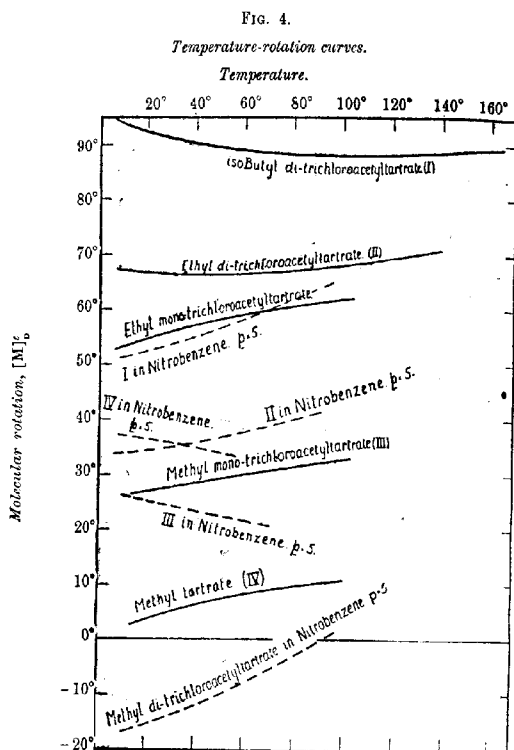
temperatures the compound is likely to solidify. Even the examination of solutions of active compounds at low temperatures will present considerable difficulty, and for these reasons it is only possible, in the meantime, to progress by piecing together such evidence as appears to bear on the question.

It is a little doubtful whether any of the temperature-rotation curves hitherto obtained are sufficiently extensive to allow of mathematical determination of their form, but a considerable

* Neglecting the slight alteration of form introduced by the shape of the density curve.

amount of cumulative, if slightly indirect, evidence can be adduced in regard to this question.

Some relevant matter is represented by the curves of Fig. 4, which have been plotted from data obtained by Patterson and Davidson (T., 1912, 101, 374). The uppermost curve is that for homogeneous *isobutyl di-trichloroacetyl*tartrate, and, as will be



observed, a distinct minimum occurs at 105° of $[M]_D + 88^\circ$. The curve for ethyl di-trichloroacetyltartrate also shows a minimum at a temperature of 54°, and having the value $[M]_D + 66^\circ$. In this case, therefore, the minimum rotation appears to move towards a higher value and a higher temperature as the series is ascended.

It is of great interest to compare these curves, in both of which the maximum rotation actually appears, so that its variation can

be traced, with some of the curves of Fig. 3, which mostly represent data obtained by P. F. Frankland and his pupils, and serve admirably to exhibit the very great effect that change of temperature may exert.

The curves shown refer to a number of compounds fairly intimately related to each other. The scale of the rotations is here very small, as will readily be apparent from the appearance of the graph for *sec*-propyl tartrate, which is included for comparison; the curvature in this instance, although so obvious in Fig. 1, is little more than perceptible.

The behaviour of ethyl dibenzoyltartrate has already been referred to, and is of especial interest. It shows a maximum negative rotation of -258° at a temperature of 63° . The other graphs, on the lower part of the diagram, give the results of observations by Frankland and Wharton (T., 1896, 69, 1309, 1583) and Frankland and Harger (T., 1904, 85, 1571). It is clear that the curve for ethyl dibenzoyltartrate is closely resembled by that for ethyl di-*o*-toluoyltartrate, and it seems almost absolutely certain that just as the maximum positive rotation of the simple alkyl tartrates of Fig. 1 moves towards a lower temperature and a greater value, and the minimum rotation of the di-trichloroacetyl tartrates (Fig. 4) moves to a higher value and a higher temperature in passing up the homologous series, so the maximum negative rotation of ethyl dibenzoyltartrate will have its analogue in a maximum negative rotation for ethyl di-*o*-toluoyltartrate, but at a lower temperature and a greater negative value. Similarly, the slopes of the curves for ethyl di-*m*-nitrobenzoyltartrate and ethyl di-*p*-toluoyltartrate suggest maximum negative rotations at still lower temperatures. The curve for ethyl di-*o*-nitrobenzoyltartrate is the most remarkable of all. The very high negative rotation diminishes with surprising rapidity as the temperature rises, the slope of the curve suggesting a maximum negative rotation at a very low temperature. The most important thing about this curve, however, is that it appears to have a point of inflection somewhere about 80° , the curvature above that temperature being certainly the opposite of that of the graphs for the analogous compounds. The form of this part of the curve is thus similar to that of ethyl tartrate between 0° and 150° , and therefore the possibility of the rotation of this compound rising* to a maximum is suggested, and from the similarity of the set of curves there would be, with almost equal probability, a maximum in the curve for the analo-

* That is, the negative rotation becomes less. It would probably be best to refer to the turning points of the curves for genetically-related compounds, as maxima or minima, irrespective of the actual sign of the rotation.

gously constituted ethyl di-*p*-nitrobenzoyltartrate at a higher temperature, and in the same way, maxima may be anticipated in each of these curves at successively higher temperatures. Further very important evidence is to be found in the admirable work of Pickard and Kenyon (T., 1911, 99, 45; 1912, 101, 620), their second paper containing two most interesting diagrams, which merit careful examination. It may particularly be noticed that maxima occur in the curves (*loc. cit.*, p. 623) for *n*-hexyl-, *n*-octyl-, and *n*-decyl-*sec*-propylcarbinol, and that, in addition, there is a point of inflection at higher temperatures, so that the curves appear to be falling to reach a minimum such as becomes much more obvious in the curves of the diagram on p. 626. Here a decided point of inflection for ethylmethylcarbinol is still apparent in *n*-propylmethylcarbinol, but develops into a minimum in *n*-butylmethylcarbinol, a minimum which gradually moves towards a higher temperature as the homologous series is ascended. Thus the variation of the rotation of an active compound with change of temperature may be, and very probably is, a *periodic* phenomenon—doubtless irregularly periodic—and several maxima and minima may be expected to occur as one or other of the groups attached to the asymmetric atom exerts a preponderating influence. Some further evidence bearing on this point will be found on p. 161.*

In passing from a given substance to one of a closely analogous type, the shape of this irregularly periodic curve alters slightly,

* Since this was written, there has appeared a paper by Frankland, Carter, and Adams (T., 1912, 101, 2470) which contains a diagram representing the optical behaviour of a splendid series of thirteen acidyl derivatives of methyl tartrate, of the utmost interest and importance in connexion with the views developed here. Methyl *o*-iodobenzoyltartrate has a comparatively low rotation which varies in such a way that there is a distinct maximum negative rotation at a temperature of about 80°. The corresponding bromo-derivative (for which the curve is not quite so satisfactory) has a greater negative rotation and a maximum occurring at about 40°. The curve for the *o*-chloro-compound shows a higher rotation with a maximum at about 50°. It appears, therefore, making some allowance for the curve of the bromo-compound, that the maximum passes to a lower temperature as the value of the rotation increases, and that this is so is very fully borne out by the appearance of the other curves shown on the diagram. The curves for the benzoyl and the *o*-toluoyl derivatives intersect in such a way as to indicate that the former is retarded on the latter. A further very important thing is to be noticed also in the diagram, namely, that the curves for the *m*-toluoyl and the *p*-toluoyl esters have the opposite curvature from the other graphs. They must almost certainly show a point of inflection in the neighbourhood of 130°, just as has been suggested for the curve for ethyl *o*-nitrobenzoyltartrate in Fig. 3 of this paper. Frankland, Carter, and Adams point out that there is a tendency for the rotation of the substances they have examined to become equalised at high temperatures, but it seems highly probable to the present writer that the curves will intersect in such a manner that at some higher temperature, say from 400° to 500°, the sequence of the rotations would be just the opposite of what it is at, say, 60°.

because the temperature, at which one of the groups attached to the asymmetric centre becomes predominant, is a little different; the one curve is somewhat retarded or advanced as the case may be, on the other, whilst the rotation produced, the amplitude, also changes by a small amount.

As has been said, no satisfactory generalisation can be arrived at regarding the curves of Fig. 1, by a consideration of rotation values for any one temperature, and it is therefore of interest to note that the ideas so far developed seem to render possible a description, at least, of the behaviour of the compounds, which shall be independent of temperature, and this in terms of the two variables phase and amplitude; thus the curve for *n*-propyl tartrate is somewhat advanced on that for ethyl tartrate, since its maximum is at a lower temperature, and, at the same time, its amplitude is greater. Similarly, the curves for allyl tartrate and for isobutyl tartrate are successively in a more advanced phase, again with an increase in amplitude. The amplitude for *sec*-propyl tartrate is still greater, but the curve is retarded on that for isobutyl tartrate, and so on, these statements describing the behaviour of the substances through the whole range of temperature examined.

It is to be observed that the sweep of most of these curves appears to be very similar, so that the period or wave-length of the temperature-rotation vibration—which, not quite in conformity with ordinary usage, may be described for convenience as the distance between a maximum and a minimum value—is possibly nearly the same for these esters, but, of course, in the meantime no definite conclusion can be arrived at in regard to this point. The only graph which does not appear to have the same sweep as the others is that for *isoamyl* tartrate, but this ester was not quite pure (see p. 175), a fact which may readily account for the slight peculiarity.

The same kind of treatment can be applied to the curves of Fig. 3, which may be referred to in connexion with the problem of position isomerism and rotation. It has been shown by P. F. Frankland that in a large number of cases the rotatory power of a set of isomerides is in the order ortho, meta, para; and that, if these are derivatives of benzoyl, the benzoyl compound itself falls, in respect of rotation, between the ortho- and the meta-derivatives. This is a regularity which even persists over a fairly wide range of temperature in many instances, but the graphs of Fig. 3 show how such a rule as this may be completely upset by alteration of temperature. At 160°, for example, we find, for some of the compounds represented, the sequence, *o*-nitrobenzoyl, benzoyl, *m*-nitro-

benzoyl, *p*-nitrobenzoyl, which is thus in complete accordance with Frankland's rule. At 110°, however, the sequence is: benzoyl, *o*-nitrobenzoyl, *m*-nitrobenzoyl, *p*-nitrobenzoyl, whilst at 40° and at 20° still other sequences are found. Since, therefore, the sequence varies for each of these different temperatures, that for any particular temperature can only have a very limited application or interest.

The whole behaviour of the compounds is summed up, however, in a qualitative sense, for any temperature, in the statement that the phase as well as the order of magnitude of the amplitude is in the sequence:

Ethyl di-*o*-nitrobenzoyltartrate,
Ethyl di-*p*-nitrobenzoyltartrate,
Ethyl di-*m*-nitrobenzoyltartrate,
Ethyl dibenzoyltartrate,

the substance first mentioned being in the most advanced phase and having the greatest amplitude.

These views can only be applied qualitatively in the meantime, and it is doubtful, in spite of all the data that have been collected, whether the experimental material is sufficiently comprehensive, in the sense of including as many of the variables as is necessary, to make it desirable to attempt a quantitative treatment of the subject. At present it need only be said that a set of graphs such as those of Fig. 1 or Fig. 3, assuming them to be periodic, suggest a rough resemblance to a series of sine curves, and possibly, as a first approximation, an expression of the form:

$$a = e^{-at} \sin (bt + c),$$

the graph of which is a curve of changing amplitude, may be proposed—mainly as a concrete example and for purposes of illustration—to represent the relation between temperature and rotation. Of the parameters in this expression, a changes the amplitude, b changes the period, whilst c alters the phase.

One other and rather important point must be referred to, namely, the relationship as regards rotation between compounds of different type. It seems to the author that there is now some hope that by a very complete examination of the rotation of active compounds it may be possible to discover the connexion between rotation and chemical constitution, even of substances differing as do glyceric acid and tartaric acid, but that is, in the meantime, merely a pious aspiration. The simpler problem, however, of the relationship between the curves for the various esters of one acid, say, tartaric acid, may be considered. The temperature-rotation curve for tartaric acid, which, very unfortunately, cannot

actually be determined, may be regarded as a fundamental graph for a large class of compounds. From data obtained by extrapolation from observations on concentrated aqueous solutions, and from analogy to the behaviour of the simple alkyltartrates, it is practically certain that the homogeneous acid will have a negative rotation at the ordinary temperature, and that this will rise with increase of temperature to reach a maximum of comparatively low value at a temperature in the neighbourhood of 200° . Substitution of the acidic hydrogens by alkyl groups—a slight change—shifts the maximum rotation to a lower temperature as the alkyl group increases in mass—at least, up to a certain point—and at the same time the amplitude increases also (Fig. 1), but the data are not full enough to allow of a complete statement even in this one case. We do not know what happens at temperatures higher or lower than those hitherto investigated. On substituting the hydroxylic hydrogens of one of these esters, say, ethyl tartrate, by acyl groups, a greater change occurs, the nature of that part of the curve within the range of ordinary temperatures alters, since the graphs for the alkyltartrates, Fig. 1, on the one hand, and those for the acyl derivatives, Figs. 3 and 4, on the other, are of different shape. The former show a temperature of maximum rotation, and the latter a temperature of minimum rotation, and this minimum again moves about to various temperatures and rotation values as slight changes are made in the substituting groups. Now if both the curves for the alkyltartrates and those for the acyl derivatives were parabolas there could hardly be any hope of deriving them from one common origin. If, however, they are periodic, the problem appears to be much simpler and capable of solution, for it seems not unreasonable to suppose that the very considerable change in constitution from ethyl tartrate to ethyl ditrichloroacetyltartrate, for instance, may have the effect of displacing the ethyl tartrate curve—in the same way that the substitution of a propyl group for the ethyl group would displace it, but to a very much greater extent—towards a higher or lower temperature so as to bring into view a minimum which would only appear in the ethyl tartrate curve within a region of temperature not easily explored.

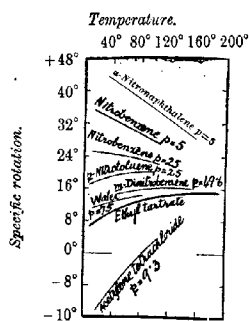
Rotation in Solution.

That the temperature of maximum rotation may play in the future an important part in connexion with the rotation of homogeneous substances will, it is hoped, be evident from what has already been said; an attempt will now be made to show that it is of equal importance in regard to the phenomena of rotation in

solution, and here again the great value of a maximum is the fact that it can be easily recognised. The maximum indicates a condition of the substance in which a certain influence—or influences—attains to a maximum, and then declines again or is outweighed by other influences, this taking place under the inter-molecular forces—the forces which produce liquefaction—at play in the compound in these particular circumstances.* If now the active substance be mixed with an indifferent solvent, the inter-molecular forces change so that the internal pressure to which the active compound is subjected assumes a different value. Under this new pressure a different temperature is required to produce that state of the

FIG. 5.
Influence of temperature on rotation
in solution.

Ethyl tartrate in various solvents.



molecule in which one of the groups attached to the asymmetric atom reaches its maximum preponderance, and since at that new temperature the molecule as a whole will have changed—in volume, for instance—the maximum rotation will have a value other than that found for the homogeneous compound, unless, of course, the internal force happen to be just the same as before when the temperature of maximum rotation should also be the same. A the solution becomes more and more dilute the internal forces gradually alter, and the temperature of maximum rotation suffers a corresponding change.

Previous work has shown (T., 1908, 93, 1843) that when ethyl tartrate is mixed with a solvent, such as water or nitrobenzene which raises its rotation at ordinary temperatures, the maximum rotation passes towards a lower temperature, but takes on a higher value as the solution becomes more dilute, and, further, that the extent to which the temperature of maximum rotation is lowered is almost directly proportional to the rise in the value of the rotation. This will be clear from the curves of Fig. 5. It will be observed that in a solvent such as acetylene tetrachloride $p=9.3$, which, at 20° , has a powerful depressing influence, the

* In the author's view, it is probable that the rotation of the free molecule of an active substance—that is, in the state of vapour—would also show maxima and minima, although this has not been experimentally verified. In the liquid condition the active molecules are subjected to new and powerful forces, and therefore the maximum rotation would probably not occur at the same temperature for the liquid as for the vapour.

rotation rises rapidly with increase of temperature, whilst in a solvent like α -nitronaphthalene, $p=5$, which greatly raises the rotation of the ester, increase of temperature diminishes the rotation with almost equal rapidity. Other solvents or the same solvents at intermediate concentrations, produce effects lying between these extremes, in such a manner that, roughly speaking, the whole series of curves gives the impression of a gradual variation of some property irrespective of the chemical composition of the solvents. If a solution in water and one in nitrobenzene have a certain rotation at some given temperature, then the temperature-rotation curves of the two solutions will be practically identical, although the concentrations may be entirely different. According to the author's working hypothesis, the internal forces against which the molecule has to expand on heating are the same or almost so, the optical behaviour being then naturally very similar. Nevertheless, although, broadly speaking, this is the case, there are minor irregularities, as will be seen on inspection of the diagram on p. 1846 of the *Transactions* for 1908.

It is to be surmised that if ethyl tartrate be dissolved in a liquid of depressing influence such as acetylene tetrachloride, the maximum will move to a higher temperature, but will at the same time assume a lower value than characterises the maximum for the homogeneous ester, and that this tendency will become more and more marked as the dilution increases, a point which will be referred to later on (p. 171). It may be noticed that ethyl tartrate seems to fall into line with the other indifferent liquids as a solvent for itself.

The influence of solvents on other rotation maxima is of a similar character to that just described. Very decided maxima were found in the temperature-rotation curves for aqueous solutions of potassium methyl tartrate, potassium ethyl tartrate, and potassium n -propyl tartrate, and these maxima move in a very distinct and interesting manner towards a lower temperature and a higher value as the solutions become more dilute, just as does the maximum for ethyl tartrate on dilution with water, but the displacement of the maximum is not so great (see Figs. 4, 5, and 6, T., 1904, 85, pp. 1121, 1123, 1125). In Fig. 2 of the present communication the curves for $p=5$ solutions of these compounds are shown, and it will be noticed that in passing from one to the other of these substances in aqueous solution the maximum rotation again moves towards a lower temperature and a higher value, just as is seen from Fig. 1 to be the case amongst the homogeneous alkyl esters of tartaric acid.

It is important now to consider the effect of solution on the

critical points of other curves, some interesting information being represented in Fig. 4 in regard to the minima in the curves for ethyl di-trichloroacetyltartrate and isobutyl di-trichloroacetyltartrate (Patterson and Davidson, T., 1912, 101, 377).

The rotation of both these esters is much depressed by solution in nitrobenzene (broken lines), and from the appearance of the curves and what has already been said, it may be regarded as almost absolutely certain that the minimum value of the rotation merely moves to a lower value and a lower temperature, just as the maximum rotation of ethyl tartrate has been observed to move towards a higher value and a lower temperature by dilution with nitrobenzene.

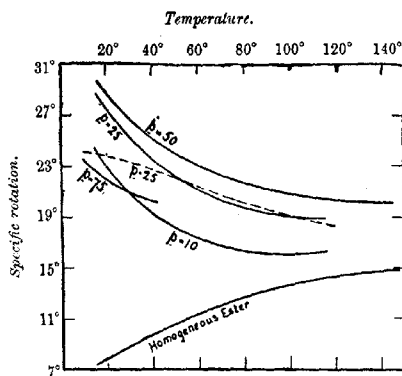
In regard to the influence of nitrobenzene as a solvent, methyl tartrate is closely analogous to ethyl tartrate. The rotation of homogeneous methyl tartrate is shown in Fig. 4. The maximum rotation has not actually been determined, but it must lie about 180° or perhaps a little higher. When dissolved in nitrobenzene ($p=5$), the ester has a high rotation, which diminishes on heating, so that in such a solution the maximum rotation has already passed to a temperature somewhere below zero; thus the minimum rotation of the di-trichloroacetyl esters is depressed and moved towards a lower temperature, whilst the maximum rotation of the simple esters is raised and also moved towards a lower temperature, when the compounds are examined in nitrobenzene solution. With the behaviour of these esters it is now most interesting to compare that of methyl mono-trichloroacetyltartrate, which, chemically, stands midway between them. The rotation of the homogeneous ester increases as the temperature rises, almost linearly (Frankland and Patterson, T., 1898, 73, 186), but from analogy to the corresponding graph for ethyl mono-trichloroacetyltartrate, which shows a distinct curvature, it is to be expected that both would tend towards a maximum at a fairly high temperature. The curve representing the behaviour of a nitrobenzene solution of the methyl ester on heating is shown on the diagram. The value of the rotation is little altered, but the temperature-coefficient is the opposite of what it is in the homogeneous ester. The rotation diminishes on heating, and it may reasonably be concluded that in this case again the maximum for the homogeneous ester is moved towards a lower temperature by solution in nitrobenzene, but without any great alteration of value. Thus, in a very broad and general sense, the influence of solution in nitrobenzene on the rotation of all these esters is of just the same character; the curve for the homogeneous ester is, as a whole, displaced towards a lower temperature, towards the left of the diagram, and by nearly the same amount, the actual

value of the rotation being lowered or raised or not much altered as the case may be, presumably according to the chemical nature of the active compound. If, then, we may regard these temperature-rotation curves as periodic, the effect of solution is to change, in the first place, the phase, and also the amplitude, of what may be called the vibration. And, further, since the sweep of these curves, both for the homogeneous esters and for their solutions, is, so far as can be judged, very similar, it may be concluded that the period of the vibration is, in practically all these instances, nearly the same.

The conception which the writer has attempted to develop in this paper bears in a very interesting manner on some results

FIG. 6.

Ethyl tartrate in quinoline (full lines), and in water (broken line).



which, at the time they were obtained, were difficult to understand or to correlate with any other phenomena. It was found that solution in water raises the rotation of ethyl tartrate, at the ordinary temperature, to a considerable extent, and that, as is usual in such cases, the rotation diminished with rise of temperature (T., 1904, 85, 1129, 1130). It was also noticed, however, that the curves for fairly dilute solutions, in addition to suggesting the passing of a maximum rotation to a lower temperature as the dilution increases, also exhibit a point of inflection at a temperature somewhere about 60°. This will be seen from the curve for water, $p=25$ 034, which is reproduced in Fig. 6. Then, later, it was observed by Patterson and McDonald (T., 1909, 95, 323) that the

influence of quinoline as a solvent on the rotation of ethyl tartrate differed considerably from anything previously recorded. The curve, even for a $p=50$ solution, starting from a high value at low temperatures, falls rapidly as the temperature increases, in such a way as to be convex with regard to the point of origin of the figure, and tending towards a minimum value in the neighbourhood of 100° . These curves, also, are shown in Fig. 6. It will be noticed that even the curve for a $p=75$ solution is convex with respect to the point of origin of the diagram, and it is therefore to be surmised that the maximum rotation of ethyl tartrate passes very rapidly towards a low temperature, on solution in quinoline, just as is the case in nitrobenzene and water and many other solvents. Only a few observations were made with the $p=75$ solution, but it is clear that the behaviour of a $p=50$ solution shows a gradual advance on that of the $p=75$ solution, of a similar character to that shown by the latter on the behaviour of the homogeneous ester. Now the general appearance of the $p=50$ curve indicates a minimum rotation at a temperature somewhere about 140° . The curve for $p=25$, because of its greater initial slope, probably has a minimum at a lower temperature and of lower value, whilst in the $p=10$ solution the minimum is distinct, and occurs at a temperature of about 94° . This case of quinoline is a specially complex one on account of the peculiar shape of the concentration curve (see T., 1909, 95, 322), which itself shows a maximum, but the appearance of the graphs suggests that just as the maximum is moved by solution in nitrobenzene towards the left of the diagram, so here—the maximum having been displaced very rapidly—a minimum is coming into view, and is also being shifted from the right of the diagram towards the left. The same kind of thing is suggested by the curves for water, but, of course, only in a much less pronounced degree. It is, therefore, not improbable that on heating homogeneous ethyl tartrate to temperatures considerably above 200° , a minimum would be discovered, or, in other words, an examination of the rotation of this substance in solution in a solvent of particular type brings into view a minimum in the curve for the homogeneous compound which, perhaps, for some reason such as the high temperature at which it occurs, and consequent decomposition, could not be directly observed.

The suggestions made in the present paper seem to correlate at least much of the most systematic work which has been done on optical activity. It becomes clear why nothing in the way of comprehensive generalisation can be expected from the comparison of rotation values made at one and the same temperature for each substance, and in particular it does away with the sharp

contrast which appeared to exist in certain respects between the rotation of homogeneous substances and the rotations of their solutions.

When an active substance is dissolved in a solvent, the general character of the periodic curve is, apparently, not very much altered, but the whole curve is displaced towards a lower or a higher temperature according to the nature of the solvent, the amplitude being considerably and the period perhaps slightly altered; or the solvent may have but little effect, in which case the maximum or minimum of the graph for the homogeneous compound occurs at exactly or nearly the same temperature in the solution whilst the amplitude is little changed or not at all.

Rotation-dispersion in Homogeneous Active Compounds.

It is of much interest now to apply these views to a problem which, since its discovery in tartaric acid by Biot (*Mém. de l'Acad.*, 1838, 15, 93) some seventy-five years ago, has always appeared to be one of particular difficulty, namely, that of anomalous rotation-dispersion. As a rule, the plane of polarisation of light of short wave-length is rotated most, but in certain cases this does not hold; instead, the rotation reaches a maximum value for waves of intermediate length, and the rotation-dispersion is said to be abnormal. This is, however, not a complete statement of the general case; it is, in fact, usually found, when the problem is investigated over a sufficient range of temperature, that at high temperatures the rotation-dispersion is normal, the violet rays being, say, most rotated; at intermediate temperatures it becomes abnormal, and at lower ones again it becomes normal once more, but in an opposite sense, the violet rays being least rotated.* Thus, by extrapolation from its solutions, Winther found "that homogeneous tartaric acid is levorotatory for all colours at low temperatures; further, that the dispersion is normal at low temperatures, but becomes abnormal at about 30°, with a maximum between red and yellow. With rise of temperature this maximum moves towards the blue" (*Zeitsch. physikal. Chem.*, 1902, 41, 187). The same peculiarity as is shown by homogeneous tartaric acid has been found by Winther in regard also to homogeneous methyl, ethyl, and *n*-propyl tartrate (*ibid.*, 177), and by Scheuer (*ibid.*, 1910, 72, 587) for ethyl diacetyl tartrate.

A considerable number of other substances have been investigated as regards this question, and in many cases the rotation-dispersion was found to be independent of the temperature and the

* I propose to call this negative rotation-dispersion, a large negative value of the rotation being regarded as less than a small negative value.

concentration. In regard to these and his own results, Winther says (*Zeitsch. physikal. Chem.*, 1902, **41**, 195, 196): "Es ist kaum wahrscheinlich, dass diese zwei Gruppen von aktiven Körpern wirklich scharf voneinander gesondert werden können; vielmehr werden sich bei weiteren Untersuchungen gleichmässige Übergänge zwischen ihnen ergeben," and this is very probable.

What is called the "rotation-dispersion coefficient" is approximately a constant for substances the dispersion of which is normal, but for such compounds as have anomalous dispersion it varies, not only in numerical value, but in sign as well. To overcome this difficulty, Winther introduced his "rational dispersion coefficient" in which the temperature of maximum rotation—the vertex of the parabolic temperature-rotation curve—played an important part (*Zeitsch. physikal. Chem.*, 1902, **41**, 207). This "rational dispersion coefficient" was found to be practically constant for methyl, ethyl, and *n*-propyl tartrate. Winther's attempt was, in fact, of just the same kind as that made by the present author a year or two later, to establish a constant relationship between the rotation values for these three esters for yellow light, and the results in both cases were of the same order (T., 1904, **85**, 765).

As has already been remarked, Winther's value for the temperature of maximum rotation was not established by experiment, but was calculated by means of a parabolic interpolation formula from experimental data obtained at temperatures up to about 60°, and his coefficient of "rational dispersion" depends expressly on the assumption "dass die maximal Temperaturen wirklich für alle Farben gleich sind" (*loc. cit.*, 209), and, considering this fact, Winther's treatment of the subject was extremely ingenious. Further, the temperature of maximum rotation which he assumed for these esters was too low, and, in addition, the value is not the same for all three.

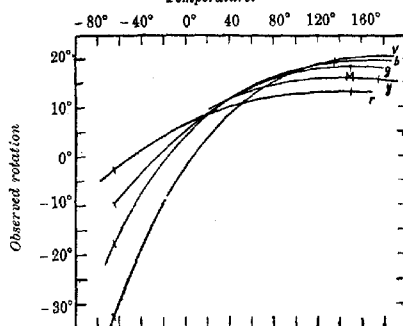
It is, then, of much interest to inquire how the temperature of maximum rotation is related to the refrangibility of the light used. In this connexion some interesting data have been supplied by Walden (*Ber.*, 1905, **38**, 366), who has examined these three esters at various temperatures for red, green, blue, and violet light, without, however, mentioning the question of maximum rotation. These data—for observed, not specific, rotation—are represented by the curves in Figs. 7 and 8, the present author's data for yellow light being added; it will be apparent that the numbers obtained by the two different observers show very good agreement. The temperature of maximum rotation in ethyl tartrate for yellow light lies at 148°, and is marked on the curve by an *M*. It will be noticed that

* The short cross-lines on the curves show the actual range of the observations.

Walden's data in only two cases extend beyond this.* Nevertheless, from the appearance of the curves and the actual numbers, which show that the difference between the observed values of the rotation at 100° and 135° becomes gradually greater and greater from red to violet, it may be concluded with almost complete certainty, that the maximum lies at a lower temperature than 148° for red light and at one progressively higher for green, blue, and violet.* The maximum probably moves from about 140° for red to about 180° for violet.

For propyl tartrate (Fig. 8), Walden's data fall on both sides of the maximum value for each colour of light, and here much the same thing applies. The maximum for red is 115° , that for yellow

FIG. 7.
Ethyl tartrate. Rotation dispersion.
Temperature.



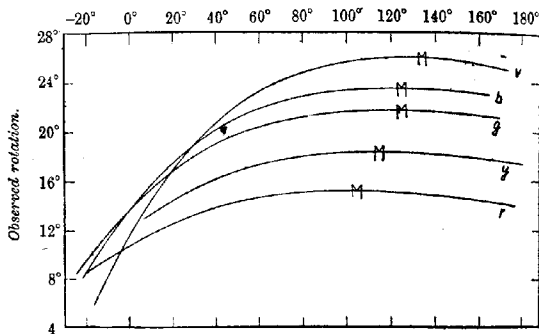
according to the determinations of the present author, is at 120° , and Walden's data give a temperature of about 125° for green and blue, and 134° for violet. The maximum thus again appears to move towards a higher temperature as the wave-length decreases.

Remembering what has already been suggested in the earlier part of this paper, regarding the curves for intimately related esters such as methyl and ethyl tartrate, for one colour of light, it would appear that the variation of rotation for different kinds of light in a single active ester is of a comparatively simple character. We seem to have, in these diagrams, a set of curves of similar type, varying in amplitude, which is greatest for violet and least for red, whilst, in addition, the curve for light of short

* Since the number of available data is small, the curves cannot be swept in with all the precision desirable.

wave-length is retarded a little on that of longer wave-length; so that there is a slight difference of phase. Naturally, therefore, since the period is apparently the same or nearly so, the curves cut one another successively within a certain range of temperature, just as a set of sine curves, retarded a little on each other, must have periods of intersection. If they were all in the same phase they would presumably all cut in one point, and the rotation-dispersion would be always normal, positive on one side of the point of intersection, negative on the other. Amongst these esters it is almost certainly always abnormal, but at temperatures from about 140° to 180° or higher, for ethyl tartrate, and 40° to 180° or higher, for

FIG. 8.
Propyl tartrate. Rotation dispersion.
Temperature.



propyl tartrate, there is a considerable separation of the curves for the different colours of light, and the abnormality is not detected. At temperatures from about $+140^{\circ}$ down to about zero or a little lower for ethyl tartrate, and from $+40^{\circ}$ down to about -40° for propyl tartrate, the curves cross each other, and the dispersion is highly abnormal. At temperatures below about 40° for methyl tartrate, zero for ethyl tartrate, and -40° for propyl tartrate, the rotation-dispersion becomes normal again, but negative (for example, ethyl tartrate at about $+8^{\circ}$, Fig. 7).

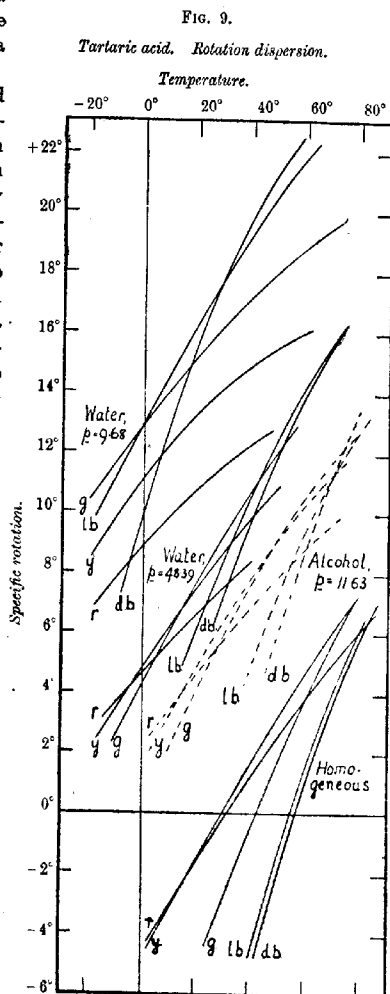
Thus in passing from one ester to another the period of intersection of the family of curves moves towards a new rotational value and a different temperature in just the same kind of way as does the maximum rotation. Abnormal rotation-dispersion is merely the natural result of the intersection of a set of curves of different amplitude retarded a little one upon the other. Such compounds

as show quite normal rotation-dispersion are probably at a temperature where, for them, a loop exists, whilst such as show abnormal dispersion are at a temperature in the neighbourhood of a node.

A point often noticed is that abnormal rotation-dispersion occurs in substances the rotation of which alters rapidly with temperature-change. The reason for this is obvious in the light of what has been said; it is between a maximum and a minimum value that the slope of the curve—the temperature-coefficient—is greatest, and it is just in this neighbourhood that the temperature-rotation curves intersect and give rise to abnormal rotation-dispersion.

Rotation Dispersion in Solution.

There remains now but one other point to consider, namely, the influence of solvents on rotation-dispersion, and for this purpose very useful data have been collected by Winther. Tartaric acid may be dealt with first. By the examination of several solutions at various temperatures for light of different colours, Winther (*Zeitsch. physikal. Chem.*, 1902, 41, 183) obtained, by extrapola-



tion, values for the specific rotation of the homogeneous compound (*loc. cit.*, 187). These data are reproduced in Fig. 9, from which it will be seen that from temperatures of about 17° downwards the dispersion of homogeneous tartaric acid is completely normal, but negative. At 17° , or nearly, the curve for red, cuts that for yellow, light, and the rotation-dispersion begins to be abnormal, the interval of temperature before the curves are free of one another again being obviously considerable. Fig. 9 shows also the curves for a fairly concentrated solution of tartaric acid in water ($p=48.39$), and it will be noticed that, in this case, the curve for red cuts that for yellow at a temperature of about -5° , the interval of abnormal dispersion extending up to about 70° . The curves thus begin to cut one another at a lower temperature than before, but the value of the rotation at the temperatures where they intersect is higher. In homogeneous tartaric acid, red cuts yellow at a rotation of -2.5° ; in the solution this happens at a rotation of $+4^{\circ}$. The uppermost curves of Fig. 9 represent the behaviour of a more dilute solution. The temperature at which red and yellow intersect lies so far outside the diagram that extrapolation becomes uncertain, but green and light blue, which in the concentrated solution cut at a temperature of 42° and a rotation of 11.1° , meet, in the dilute solution, at a temperature of -2° and a rotation of 12.7° .

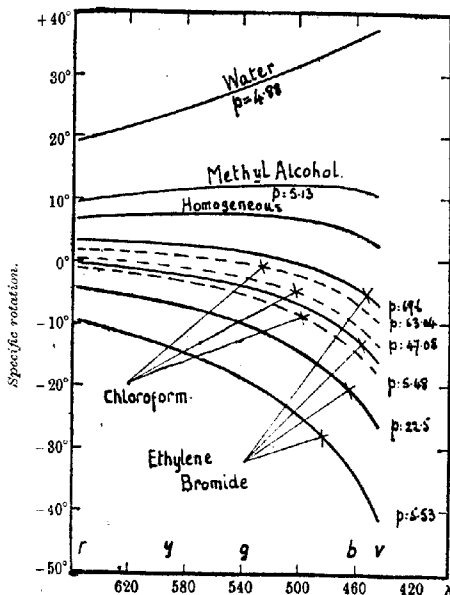
This behaviour is thus altogether in agreement with what was to be expected. It is a fact that solution in water raises the rotation of tartaric acid, and from analogy to the behaviour of the esters of tartaric acid, the maximum, which will almost certainly be found to exist in the temperature-rotation curve for tartaric acid if means can be found to investigate the point, will move towards a lower temperature and a higher value as the result of this solution. In other words, that part of the temperature-rotation curve for the homogeneous substance in the neighbourhood of the maximum, comes, when the acid is dissolved in water, into the region of ordinary temperatures. It has just been shown, however, that in the neighbourhood of the maximum rotation, the rotation-dispersion becomes more nearly normal. Therefore, when the maximum is brought by solution into the region of ordinary temperatures, the dispersion at these temperatures, in solution, becomes normal.

Again, whilst water raises the rotation of tartaric acid to a considerable extent, alcohol has only a slight influence in the same direction. It is therefore to be expected that the rotation-dispersion in alcohol should be much the same as in the homogeneous active substance, and this is actually found to be the case. In Fig. 9 are shown also rotation-temperature curves for tartaric acid in alcohol,

$p=11.63$, which may be compared with those for the homogeneous acid. In the alcoholic solution it will be noticed that at low temperatures, that is, below 10° , the dispersion is normal but negative. The curves begin to cross at about 14° when the rotation is 3.8° , and the interval of abnormal dispersion extends up to a temperature in the neighbourhood of 80° . For the homo-

FIG. 10.

Rotation dispersion.

Ethyl tartrate in various solvents at 20° .

geneous acid, as has already been said, the crossing of the curves begins at a higher temperature and a lower rotation value, and extends also to a higher temperature. The sets of curves are much alike, and are altogether consistent with the idea that solution in alcohol has the effect of shifting the temperature-rotation curves of tartaric acid towards a slightly lower temperature and a slightly higher rotation value.

It might, however, be objected that the maximum rotation-value for tartaric acid is not known experimentally, and therefore it

will be well to examine one or two other cases. Again, valuable data are supplied by Winther, and are represented in Fig. 10 as dispersion-rotation curves for a temperature of 20° .^{*} In dilute solution in water the rotation is high, the dispersion normal and positive; in methyl alcohol the rotation is not so much raised as in water, and the dispersion has become abnormal; chloroform gradually depresses the rotation of ethyl tartrate as the dilution increases, and we find that the abnormality has just disappeared in the most concentrated solution, but the dispersion has become negative; in ethylene bromide, which still further depresses the rotation of the ester, the dispersion may be said to have become more normal and more negative. Now it is known definitely that the maximum rotation of homogeneous ethyl tartrate moves, on dilution with water and such other solvents as raise the rotation, towards a lower temperature and a higher value, that is, into the region of ordinary temperatures, and in correspondence with this, for the reason which has been given, the dispersion in aqueous solution becomes normal in the neighbourhood of 20° . In methyl alcohol, which does not so much raise the rotation of the ethyl tartrate, the maximum is slightly shifted towards a lower temperature, and some crossing of the curves is apparent at 20° ; for homogeneous ethyl tartrate the maximum is still more to the right, so that 20° is a temperature at which the most marked intersection of the curves takes place. In chloroform, however, with its depression of the rotation, the maximum is, presumably, moved out further towards the right, towards a higher temperature and a lower value, and therefore all the crossing of the curves takes place at higher temperatures than 20° , so that in Fig. 10 the dispersion, in this solvent, has become normal but negative. In ethylene bromide the same thing occurs, but in a more marked manner; the region of crossing of the curves has passed, along with the maximum rotation, to a still higher temperature, with the result that the rotation-dispersion curves become yet more negatively normal. The set of curves of Fig. 10 thus seems to form a complete whole; some property appears to progress gradually throughout the diagram irrespective of the solvent used, the curvature slowly changes from that of the lowest graph to the opposite shape in the uppermost, the rotation-dispersion changes from negative normality in ethylene bromide through abnormality to positive normality in water, and it seems, at least to the present author, that there can surely be little, if any, doubt that this is due to displacement, as the result of solvent action, of the whole set of temperature-rotation curves for the homogeneous ester, towards a

^{*} Unfortunately, these have not been determined over a range of temperature.

lower temperature in water and a higher temperature in ethylene bromide.

The region of intersection of the family of curves for a given active compound moves to a different temperature, and assumes a new rotational value, so far as the experimental data allow of a judgment, in just the same way that the maximum rotation is displaced, by mixture with the same solvents.

It is necessary here to say a few words concerning Winther's position in regard to rotation-dispersion, in order to emphasise the very fundamental difference between it and the views developed in this paper. Winther was very clear on what may be called the empirical side of this question, but he established his "rational dispersion coefficient" on the idea, at least as a first approximation, that the temperature of maximum rotation was a constant, independent of the colour (for one and the same compound), independent also of the solvent, and independent even of substance, within the limits of a homologous series (*Zeitsch. physikal. Chem.*, 1902, 41, 179; 1903, 45, 334, 340 ff.; 1905, 52, 206). "Die Mittelwerte variieren für die ganze Weinsäuregruppe, die Lösungen mitgenommen, von 137—149°" (*ibid.*, 1903, 45, 377). All these assumptions are demonstrably incorrect. Especially does the temperature of maximum rotation vary with solution in some powerful solvent like nitrobenzene or water, passing from 175° its value in the homogeneous ester to temperatures well below zero already in only moderately dilute solutions in these solvents. From the present author's work on this subject it would seem almost certain that in a solvent like ethylene bromide, with a very strong depressing influence, the temperature of maximum rotation will move towards a higher temperature but a lower value, although the point has not been verified by direct experiment. It is therefore of peculiar interest that Winther finds by his interpolation method for propyl tartrate in ethylene bromide the following temperatures of maximum rotation at the concentrations specified (*ibid.*, 1903, 45, 340).

p.	l.
74.71	136°
45.00	165
15.29	197

The temperature of maximum rotation appears to move towards a higher temperature as the dilution increases, that is, as the depressing influence of the solvent increases, and this must be regarded as very strong evidence in favour of what has been developed in this and other papers in regard to the variation of the temperature of maximum rotation in different solvents and on dilution. Winther, however, for the second time in his work,

deliberately rejects this information, and developed his views instead, as has been remarked, on the assumption of a constant value for the temperature of maximum rotation, so that his treatment is the very opposite of that of the present communication, in which an attempt has been made to show that it is exactly owing to the variability of the maximum—the displacement of the whole temperature-rotation curve—that most of the puzzling phenomena of optical activity are, in fact, due.*

It may be pointed out in conclusion that the object of this paper is not primarily the development of a theory. The subject-matter is indeed quite independent of any theory, except in minor points, such as in the suggestion that temperature-rotation curves are in reality periodic. A fair amount of evidence has been adduced for thinking that this is so, but if it were not the case, it still remains a fact that there is a maximum at a certain temperature in many curves; that this maximum is displaced in a certain way in passing from one member to another of a homologous or closely related series of compounds; that this maximum is found at different temperatures as the concentration is varied in a given solvent, but having a different value, and generally at different temperatures for the same concentration in different solvents; that the temperature of maximum rotation, of some compounds at least, is different for different colours of light, and this seems to be sufficient to account for the phenomena of rotation dispersion; that the region of intersection of the curves for different colours of light is displaced, as the result of solution, in just the same manner as is the maximum rotation, which appears to account for most, if not all, of the known phenomena of rotation dispersion in solution; all these statements are facts, whether the temperature-rotation curves are periodic or are parabolas, but in the former, and much more probable case, it is possible to see a relationship between the curves for substances of different type, and in the latter it is, at least, more difficult. The recognition of the displacement of a fundamental type of curve enables us to bring into one general scheme all the diverse phenomena of optical activity.

These matters also do not necessarily involve a discussion of the mechanism of the process to which the phenomena mentioned are due; it may be possible to explain all these facts in terms of the very popular, if somewhat vague—or because somewhat vague!—ideas, association, or complex formation—solvation—and it would be exceedingly interesting if some exponent of these ideas would

* It may be remarked that the expression on p. 156, by alteration of the parameters, could be made to cover the whole behaviour of active compounds, including wave-length of the light used and the influence of the solvent.

attempt to show that it is possible to formulate a consistent scheme, based on them, and capable of withstanding even the first breath of criticism, but to the author it appears that the potentialities of the asymmetric carbon atom and of the most simple physical conception of those inter-molecular forces to which liquefaction is due,* are ample to account for all the observed behaviour.

However that may be, the chief claim which the present paper makes is not to the establishment of a theory, but one much more important, namely, the recognition of the above-mentioned facts and their inter-relationship.

EXPERIMENTAL.

Rotation Data.

(Numbers marked with an asterisk are extrapolated or interpolated.)

Ethyl Tartrate.—The data for this ester were the same as given in T., 1908, 93, 1852.

.....	17.8°	20.0°*	35.3°	60.4°	92.9°	124.0°	143.0°	160.0°	175.0°	200.0°*
c_{D}^{20} (100 mm.)	+9.222	9.5	11.174	18.318	15.022	15.774	15.926	15.88	15.74	15.18
$[\alpha]_D^{20}$..	7.64	7.87	9.89	11.45	13.28	14.35	14.75	14.95	14.99	14.87
M_D^{20} ..	15.74	16.21	19.34	23.58	27.35	29.56	30.38	30.79	30.83	30.63

n-Propyl Tartrate.

The ester used boiled at 173—174°/17 mm.

.....	16.5°	20.0°*	45.5°	77.7°	111.2°	123.0°	133.2°	147.2°	161.0°	173.0°
n_D^{20} ..	1.1407	1.1375	1.1127	1.0819	1.0487	1.0372	1.0272	1.0128	0.9990	0.987
c_D^{20} (100 mm.)	13.94°	14.17°	16.16°	17.83°	18.26°	18.27°	18.20°	18.05°	17.75°	17.47
$[\alpha]_D^{20}$..	12.22	12.54	14.52	16.48	17.44	17.62	17.72	17.82	17.77	17.70
M_D^{20} ..	23.00	29.34	33.98	38.56	40.81	41.23	41.47	41.70	41.58	41.42

Densities determined:

t	15.26°	39.9	75.8	132.5	167.0
d	1.1420	1.1185	1.0836	1.0279	0.9927

sec-Propyl Tartrate.

The ester was prepared by Fischer and Speier's method. It boiled at 137—158°/16 mm.*

t	15.3°	20.0°*	49.7°	73.0°	118.0°	136.0°	144.5°	155.0°	173.0°
n_D^{20} ..	1.1145	1.1100	1.0810	1.0580	1.0124	0.9934	0.9845	0.9734	0.9535
c_D^{20} (100 mm.)	22.9°	23.36°	24.5°	25.04°	25.01°	24.66°	24.405°	24.11°	23.48°
$[\alpha]_D^{20}$..	20.55	20.90	22.66	23.67	24.69	24.82	24.79	24.77	24.63
M_D^{20} ..	47.97	48.91	53.02	53.88	57.77	58.07	58.00	57.96	57.63

* Which, after all, may embrace that departure, in moderately concentrated solutions, from the laws which are only valid for infinitely dilute solutions, and which is often regarded, without any proper reason, as an indication of association.

174 PATTERSON: AN ATTEMPT TO HARMONISE, QUALITATIVELY,

Densities determined:

ρ	13.66°	40.6°	79.75°	15.0°
d	1.1162	1.0899	1.0513	0.9789

Allyl Tartrate.

The ester was prepared by boiling tartaric acid with allyl alcohol for some hours, and distilling off the excess of alcohol as far as possible. Fresh alcohol was then added, the mixture again boiled for several hours, the alcohol distilled off, and the ester fractionated. It boiled at 191°/20 mm., 182°/15 mm., and 171°/10 mm.

For hydrolysis 2.0894 grams required 13.8 c.c. of 1.337*N*-potassium hydroxide. Theory demands 13.6 c.c.

t	15.6°	20.0°*	33.2°	71.5°	106.6°	18.4°	131.6°	148.2°	168.0°
d	1.1988	1.1941	1.1813	1.1435	1.1097	1.1956	1.0842	1.0672	1.0475
α_D^{20} (100 mm.)	18.314°	18.57°	19.163°	20.522°	20.706°	18.32°	20.40°	20.024°	19.31°
$[\alpha]_D^{20}$...	15.28	15.52	16.23	17.95	18.66	15.32	18.82	18.76	18.44
$[M]_D^{20}$...	35.15	35.70	37.32	41.28	42.92	35.24	43.29	43.15	42.41

Densities determined:

t	26.6°	38.5°	48.75°	80.0°	148.5°
d	1.1874	1.1757	1.1654	1.1350	1.0669

isoButyl Tartrate.

Two different specimens of *isobutyl tartrate* were used, one prepared from the dextro-acid and the other from the laevo-acid. The rotation values agree almost exactly. The boiling point of both was 185°/21 mm., and the melting point 73—74°.

isoButyl d-Tartrate.

t	20.0°*	97.5°	80.6°	69.1°
d	—	1.0106	1.0257	1.0362
α_D^{20} (100 mm.) ...	+19.8°	+20.66°	+20.56°	+20.55°
$[\alpha]_D^{20}$	17.75	+20.44	+20.03	+19.83
$[M]_D^{20}$	46.5	+53.55	+52.47	+51.96

Densities determined:

t	75.2°	86.2°	97.7°
d	1.0309	1.0206	1.0105

isoButyl l-Tartrate.

t	78.6°	97.5°	121.3°	148.7°
d	1.0295	1.0115	0.9887	0.9676
α_D^{20} (100 mm.) ...	-20.60°	-20.64°	-20.34°	-19.64°
$[\alpha]_D^{20}$	-20.01	-20.40	-20.57	-20.29
$[M]_D^{20}$	-52.43	-53.45	-53.9	-53.17

Densities determined:

<i>t</i>	98.2°	108.6°	130.2°	146.0°
<i>d</i>	1.0107	1.0075	0.9899	0.9649

Diisoamyl Tartrate.

This ester was prepared, by the hydrogen chloride saturation method, from a so-called *isoamyl* alcohol supplied by Kahlbaum, having a rotation of -2.262° in a 2-dcm. tube at 15.5° . The ester boiled at $195^\circ/16$ mm.

<i>t</i>	15.6°	20.0°*	40.7°	92.0°	131.2°	157.0°	175.0°
<i>d</i>	1.0689	1.0586	1.0400	0.9943	0.9596	0.9365	0.9205
α_D^{20} (100 mm.) ...	12.077°	12.45°	13.995°	15.992°	16.047°	15.722°	15.368°
$[\alpha]_D^{20}$	11.32	11.78	13.46	16.01	16.72	16.79	16.69
$[\text{M}]_D^{20}$	32.88	34.02	39.04	46.43	48.49	48.69	48.40

Densities determined:

<i>t</i>	14.75°	43.3°	77.9°	167.0°
<i>d</i>	1.0631	1.0379	1.0080	0.9278

Disec-octyl Tartrate.

This ester was prepared by heating a mixture of tartaric acid and *sec.*-octyl alcohol in a flask on the water-bath and passing dry hydrogen chloride through the liquid for about four days. The excess of octyl alcohol was then distilled off, fresh alcohol added, and the current of hydrogen chloride again passed into the liquid for about five days more. The octyl alcohol was then removed by distillation, the residue shaken with sodium carbonate solution, dissolved in ether, this solution dried with calcium chloride, the ether removed, and the ester distilled under diminished pressure. The octyl tartrate boiled at $239^\circ/15$ mm. and at $194^\circ/3$ mm.

t	18.4°	20.0*	41.0°	74.4°	107.5°	133.0°
d	1.0055	0.9992	0.9825	0.9557	0.9291	0.9087
α_D^{20} (100 mm.) ...	10.256°	10.4°	11.18°	11.98°	12.37°	12.34°
$[\alpha]_D^{20}$	10.25	10.45	11.38	12.54	13.31	13.58
$[\text{M}]_D^{20}$	38.33	39.09	42.56	46.69	49.78	50.77

t	159.0°	173.0°	179.0°	131.5°	200.0*
d	0.8880	0.8766	0.8719	0.9099	0.8549
α_D^{20} (100 mm.)...	12.21°	11.98°	11.89°	12.36°	11.35°
$[\alpha]_D^{20}$	13.75	13.67	13.64	13.60	13.28
$[\text{M}]_D^{20}$	51.41	51.11	51.00	50.88	49.65

Densities determined:

<i>t</i>	18.6°	36.45°	53.1°	70.65°	100.1°
<i>d</i>	1.0003	0.9861	0.9727	0.9587	0.9353

sec.-Octyl tartrate was first prepared by McCrae (T., 1902, 81, 1221; see also T., 1901, 79, 1103) by a method suggested by Patterson and Dickinson (T., 1901, 79, 280). McCrae gave as the molecular rotation of the compound $[\text{M}]_D^{25} + 22.55^\circ$, and states that on account of the insolubility of tartaric acid in octyl alcohol, the hydrogen chloride method cannot be used in this case. The rotation of the ester examined in this investigation was very considerably higher than that quoted by McCrae, and in order to ascertain which observation was correct a new preparation was on the point of being started when a paper appeared by Pickard and Kenyon (T., 1911, 99, 67) containing a description of di- β -octyl *d*-tartrate. These authors prepared their ester by Patterson and Dickinson's method from dimethyl and diethyl tartrate. They give the boiling points as $202\text{--}210^\circ/6\text{ mm.}$, and the rotation as $[\text{M}]_D^{25} + 41.1^\circ$, which agrees fairly well with the above estimation, but not at all with that recorded by McCrae, whose preparation was therefore contaminated with a considerable proportion of ethyl octyl tartrate. The discrepancy between the rotation of Pickard and Kenyon and that of the present author may perhaps be ascribed partly, at least, to a slight difference in the rotation of the octyl alcohol used.

*Dibenzyl Tartrate.**

Freundler (*Ann. Chim. Phys.*, 1894, [vii], 3, 448) records two unsuccessful attempts to prepare this compound, the first by passing hydrogen chloride through a mixture of tartaric acid and benzyl alcohol, and the other by heating silver tartrate with benzyl chloride. He remarks that benzyl tartrate decomposes on distillation. Nevertheless, benzyl tartrate is quite easily obtained by heating tartaric acid and benzyl alcohol for some hours in a distilling flask fitted to a condenser. In quite a short time all the acid passes into solution, and water begins to separate. If the liquid be kept gently boiling, water and a little benzyl alcohol pass over. The mixture may then be distilled under diminished pressure until all the alcohol has passed over, or the latter may be removed by a current of steam. The former method is the simpler, since the residue can be distilled immediately without further treatment, but the distillation must be carried out at a low pressure of about 4 mm., when the substance boils at about $250\text{--}270^\circ$. Since the distillation can only be done on rather small quantities, it is difficult to get an accurate determination of this constant. The

* Medinger (*J. pr. Chem.*, 1912, [iii], 86, 345) describes the preparation of benzyl tartrate (a viscid, yellow oil) by heating benzyl alcohol, tartaric acid, and potassium hydrogen sulphate.

compound melts somewhat indefinitely in the neighbourhood of 50°. It forms a solid rather resembling fat, consisting of very fine hair-like crystals. It can be crystallised from ether, ethyl acetate, or benzene, but the crystals formed are so fine that it seems impossible to separate them from the mother liquor, either by the aid of the pump or on porous plate; it separates from benzene as a remarkably close imitation of a jelly.

For hydrolysis, 1.7558 grams of the distilled ester required 23.14 c.c. of 0.4625*N*-potassium hydroxide. Theory demands 23.01 c.c.

Rotation Data.

<i>t</i>	36.0°	21.2°	51.5°	71.5°	93.0°	116.0°	138.0°	170.8°	15.0°
<i>d</i>	1.2360	1.2493	1.2220	1.2038	1.1845	1.1639	1.1443	1.1089	1.2550
<i>c</i> (100 mm.)	25.05°	24.865°	25.535°	26.0°	23.005°	25.61°	25.045°	23.85°	24.17°
<i>[α]_D</i>	20.27	19.50	20.90	21.6	21.95	22.0	21.89	21.49	19.26
<i>[M]_D</i>	66.89	64.36	68.96	71.28	72.45	72.62	72.23	70.92	63.56

Densities determined:

<i>t</i>	72.2°	96.8°	152°	167°
<i>d</i>	1.2036	1.1808	1.1322	1.1184

ORGANIC CHEMISTRY DEPARTMENT,
UNIVERSITY OF GLASGOW.

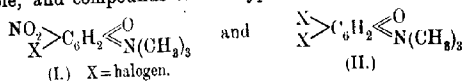
XXII.—Quinone-ammonium Derivatives. Part II. Nitro-haloid, Dihaloid and Azo-compounds.

By RAPHAEL MELDOLA and WILLIAM FRANCIS HOLLELY.

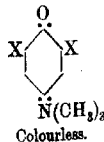
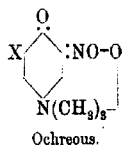
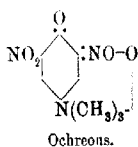
The products of the extreme methylation of the picramic acids by methyl sulphate in the presence of alkali hydroxide have been shown in a former paper (T., 1912, 101, 912) to be dinitro-derivatives of trimethylammonium-benzoquinone. These compounds are of an ochreous colour in the anhydrous "quinonoid" form, that from isopicramic acid being red in the hydrated form, for which a quinole structure has been suggested (*loc. cit.*, p. 918). The relationship of these compounds to the iminazolium compounds and iminazolones described in a series of previous communications to the Society has also been indicated (*loc. cit.*, p. 921). The research has accordingly been extended with the object, in the first place, of obtaining further evidence with respect to the influence of the substituents on the colour of the compound, and

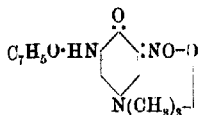
in the next place, with the object of preparing, if possible, quinone-ammonium derivatives containing an asymmetric nitrogen atom for comparison with the iminazolium compounds and iminazolones referred to. The first line of investigation has been successfully followed up, and the results are made known in the present paper. The second series of experiments have presented unforeseen practical difficulties, owing to the great tendency on the part of the amino-group in the aminophenols and their derivatives to undergo complete alkylation instead of partial substitution. This branch of the research is being continued.

The preparation of the halogen derivatives of the quinone-ammonium compounds has been much facilitated by the discovery that the nitro-groups in the nitro-derivatives are quite readily brought under the control of reducing agents with partial or complete reduction. The complete or partial replacement of these groups by halogens by the diazo-reaction has thus been made possible, and compounds of the types:

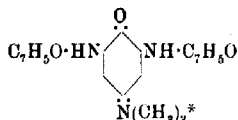


have been prepared. The dependence of the colour of these compounds upon the presence of the nitro-group is conclusively established by the fact that compounds of type I are ochreous, and those of class II colourless. The constitution of these haloid derivatives, so far as concerns the positions of the substituents, is in all cases established by the constitution of the parent compounds. The complete disappearance of colour when both nitro-groups are replaced by halogens may, so far as the chemical evidence goes, be fairly interpreted by assigning a different constitution to the nitro-derivatives. This possibility, which was indicated in our last paper, receives further support from the present extension of the research. Thus, taking the series from isopicramic acid, which has been the more completely investigated, it will be seen that no ortho-quinonoid structure is possible in the case of the dihaloid derivatives. The association of colour as a property with the possibility of assuming meta cross-linking thus appears to be a justifiable hypothesis, it being understood that the term "quinonoid" covers both ketonoid and cross-linked forms:



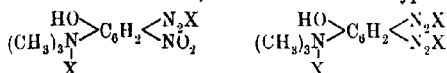


Ochreous.



Colourless.

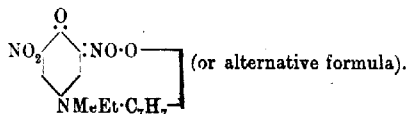
Not the least interesting character of the amino- and diamino-derivatives of the quinone-ammonium compounds is the readiness with which they can be diazotised. The di- or bisdi-azonium salts, being formed in acid solutions, are no doubt of the types:



X = acid radicle.

Direct evidence of the existence of compounds of these types is furnished by the fact that the actual salts of the corresponding azo- and bisazo-compounds have been isolated. These azo-derivatives belong to a new type, and as they promise to be of exceptional interest, their detailed study is being continued.

We may take the present opportunity of placing preliminarily upon record the successful isolation of the first compound of the present series containing an asymmetric nitrogen atom, namely, the quinone-ammonium derivative from isopicramic acid containing the radicles methyl, ethyl, and benzyl attached to the same nitrogen atom:



This compound should be resolvable into optical isomerides, but its intractable character has hitherto offered insuperable obstacles to its investigation, and much experimental work will be necessary before we can hope to accomplish a successful resolution.

EXPERIMENTAL.

The partial reduction of 2:6-dinitro-4-trimethylammonium-1-benzoquinone (T., 1912, 101, 927) † is readily effected by gently boiling the substance with dilute ammonia and ammonium sulphide until it passes completely into solution and no longer crystallises

* Described in last paper, *loc. cit.*, p. 929.

† The third alternative formula given in the above paper (p. 927) is erroneously printed. The para-N atom should be singly and not doubly linked to the benzene nucleus.

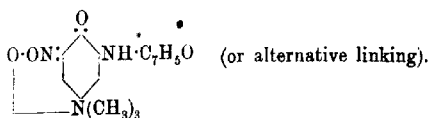
out on cooling. The solution, on acidification with hydrochloric acid, and after removal of sulphur by filtration, contains the very soluble chloride of the nitroamino-derivative. Neither the salts nor the free base could be isolated on account of their extreme solubility in water, so the solution was made alkaline by sodium hydroxide and agitated with benzoyl chloride, as in the Schotten-Baumann process. The resinous mass thus formed was collected, washed with water, and purified by solution in hydrochloric acid and reprecipitation by ammonia. After two crystallisations from hot water, the compound had a constant decomposing point of $282-283^{\circ}$, showing signs of darkening from about 265° . It crystallises in long, slender, golden needles:

0.1033 gave 0.2299 CO_2 and 0.0508 H_2O . $\text{C}=60.70$; $\text{H}=5.46$.

0.1012 „ 11.9 c.c. N_2 (moist) at 18.5° and 751 mm. $\text{N}=13.39$.

$\text{C}_{16}\text{H}_{17}\text{O}_4\text{N}_3$ requires $\text{C}=60.92$; $\text{H}=5.44$; $\text{N}=13.33$ per cent.

From its mode of formation the compound is 6-nitro-2-benzoyl-amino-4-trimethylammonium-1-benzoquinone:



Nitro-haloid Derivatives

The reducibility of one of the nitro-groups having been proved to be possible by the isolation of the above compound, experiments were undertaken with the object of introducing a halogen atom in place of the amino-group. The diazotised nitroamino-compound was found to be readily amenable to treatment by the Sandmeyer process, but in the case of the chloro- and bromo-derivatives the products were too soluble in water to allow of their separation from the inorganic salts contained in the solution. The iodonitro derivative was prepared by reducing the dinitroquinone-ammonium compound with ammonium sulphide as described above, and diazotising the acidified solution with sodium nitrite. On mixing the solution containing the diazonium salt with a concentrated solution of potassium iodide and completing the reaction by the application of heat in the usual way, the iodonitro-compound separates on cooling as a dense, microcrystalline deposit. The latter was collected, washed with water, then with dilute sodium hydroxide to remove free iodine, and then again with water. After crystallisation from hot water, in which the compound is fairly soluble,

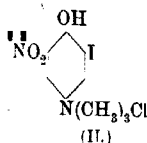
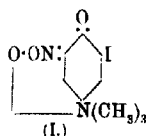
ochreous needles were obtained, which had no definite melting point, but which commenced charring about 200° and remained unchanged up to 300° . The air-dried substance undergoes no loss on heating, and proved on analysis to be the anhydride:

0.1722 gave 12.75 c.c. N_2 (moist) at 18° and 766.8 mm. $N=8.63$.

0.2564 „ 0.1849 AgI. $I=38.95$.

$C_9H_{11}O_3N_2I$ requires $N=8.69$; $I=39.42$ per cent.

The compound is accordingly 2-iodo-6-nitro-4-trimethylammonium-1-benzoquinone (I):



The presence of two nitro-groups in the original dinitroquinone-ammonium compound so far enfeebls the basicity of the molecule that no stable salts could be isolated (T., 1912, 101, 928). The substitution of iodine for one of the nitro-groups restores the basic character of the compound to a sufficient extent to enable it to form stable salts, the transition from the coloured form to a colourless salt (No. II above) on the breaking down of the quinonoid structure being most striking. The chloride was prepared by dissolving the iodonitro-compound in hot dilute hydrochloric acid and allowing the solution to cool, when the salt separates in small, silvery scales, showing prismatic colours in the solution:

0.1986 gave 13.1 c.c. N_2 (moist) at 19° and 771.3 mm. $N=7.70$.

0.3236, decomposed in aqueous solution with silver nitrate, gave

0.1324 AgCl. $Cl=10.11$.

$C_9H_{12}O_3N_2ClI$ requires $N=7.82$; $Cl=9.89$ per cent.

An attempt to prepare the nitrate led to the discovery that the iodine atom in the iodonitro-compound is readily displaceable by the nitro-group. The solution obtained by decomposing the chloride with silver nitrate and filtering off the silver chloride gave, on evaporation, a substance which crystallised in long, yellow needles, which on analysis were found to contain 11.96 per cent. of nitrogen, the nitrate requiring 10.91 per cent. The colour of this salt and the high percentage of nitrogen pointed to the conclusion that the free nitric acid was re-nitrating the compound with the liberation of iodine. This conclusion was verified by several experiments, the salt obtained by dissolving the iodonitro-compound in dilute nitric acid, and which consists of colourless needles, even after drying

in the air, was found to contain 12.2 per cent. of nitrogen. The iodonitro-compound dissolves also in nitric acid (D 1.42), with the immediate liberation of iodine and the formation of the original dinitroquinone-ammonium compound.

2-Bromo-6-nitro-4-trimethylammonium-1-benzoquinone.

As already stated in the introductory portion of this paper, the solubility of the bromonitro-derivative in water has prevented its preparation through the nitroamino-compound and the diazo-reaction. We have, however, succeeded in preparing a small quantity of the substance by another method, which, although leaving much to be desired in the way of yield, appears to be worthy of further elaboration. This method consists in methylating bromonitro-*p*-aminophenol prepared as described below.

Monobenzoyl-*p*-aminophenol* is dissolved in a small quantity of hot glacial acetic acid, and the solution mixed with an acetic acid solution of bromine containing one molecular proportion of the latter. The solution is allowed to remain for some hours at the ordinary temperature and then heated in order to complete the reaction and to expel hydrogen bromide. The crude substance is precipitated in a granular state by pouring the hot acetic acid solution into cold water with brisk agitation. Purification is effected by crystallisation from dilute alcohol with animal charcoal, the pure compound crystallising in white needles, melting at 184—185°:

0.0914 gave 3.9 c.c. N_2 (moist) at 19° and 769.4 mm. $N = 4.96$.

$C_{13}H_{10}O_2NBr$ requires $N = 4.79$ per cent.

From its mode of formation the compound is no doubt the benzoyl derivative of the 2-bromo-4-aminophenol described by Hölz (*J. pr. Chem.*, 1885, [ii], 32, 65). Confirmation of this is furnished by the behaviour of the compound on nitration, when it yields a bromonitro-derivative analogous to isopicramic acid in all its properties. In order to nitrate the bromo-compound, the latter is suspended in well-cooled glacial acetic acid and a mixture of fuming nitric acid (D 1.5) with an equal volume of acetic acid, this mixture being also well cooled, is gradually added with constant stirring. In a short time the bromo-compound is converted into the nitro-derivative, and the contents of the beaker solidify to a crystalline pulp. At this stage the addition of nitric acid must at once be stopped, as the product dissolves in excess of

* The preparation of this substance is described in a paper communicated to *The Chemical World* for October, 1912; Vol. I., p. 327.

acid with complete decomposition. On completion of the nitration the pulpy mass is immediately stirred into water containing ice, collected, washed, and dissolved in hot dilute ammonia, from which solution the ammonium salt crystallises out, on cooling, in orange needles, similar in appearance to the ammonium salt of benzoyl-isopicramic acid. The pure compound, obtained from the ammonium salt by decomposing the latter with dilute hydrochloric acid, is but sparingly soluble in boiling alcohol. It crystallises from this solvent in brilliant, golden-yellow scales, melting at 257° :

0.2481 gave 16.97 c.c. N_2 (moist) at 13° and 768.9 mm. $N=8.18$.

0.2234 „ 0.1255 AgBr. $Br=23.90$.

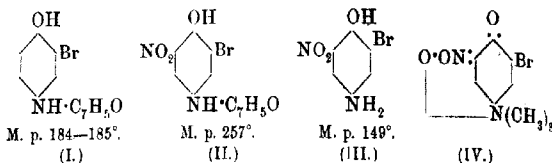
$C_{13}H_5O_4N_2Br$ requires $N=8.31$; $Br=23.72$ per cent.

The hydrolysis of the above compound was effected by heating, with excess of concentrated sulphuric acid until a drop of the solution, on dilution with water, on a watch-glass gave no indication of the presence of undecomposed substance. A somewhat high temperature is required for the hydrolysis, and the sulphuric acid solution must be kept for some time just at the point when it shows indications of fuming, as in the corresponding process for the hydrolysis of benzoyl-isopicramic acid. There is much loss at this stage, owing to secondary decomposition, and we have not been enabled to obtain better results by using diluted acid or with the acetyl derivative instead of the benzoyl derivative. Should this bromonitro-*p*-aminophenol prove to be of special value in the future extension of the research, as seems likely to be the case, we hope to be able to revise and improve the process for preparing it. When the hydrolysis was complete, the sulphuric acid solution was allowed to cool, poured into cold water, filtered to remove benzoic acid and resinous impurity, and neutralised with ammonia. After remaining for some hours the crude product which separated was collected, washed with water, and purified by repeated solution in cold hydrochloric acid, filtration, and reprecipitation by neutralisation with ammonia until it dissolved in hydrochloric acid without leaving any residue. The bromonitro-*p*-aminophenol thus obtained crystallises from dilute alcohol in deep reddish-brown scales or needles, melting at 149° . It is both phenolic and basic, forming colourless salts with acids, and dissolving in sodium hydroxide solution with an orange colour. The presence of bromine was proved qualitatively:

0.1423 gave 14.3 c.c. N_2 (moist) at 16.5° and 769.5 mm. $N=11.83$.

$C_6H_5O_3N_2Br$ requires $N=12.02$ per cent.

The formulæ of these compounds, which do not appear to have been described before, are given below:



2-Bromo-6-nitro-4-trimethylammonium-1-benzoquinone (No. IV above) was prepared by methylating the bromonitrophenol with methyl sulphate and sodium hydroxide solution in the usual way. The product is more soluble in water than the corresponding dinitro-compound, so that the methylation must be carried out in a minimum quantity of water. Purification was effected by dissolving the compound in hydrochloric acid, filtering, and adding ammonia in excess to the acid solution. As the solution cools, the substance crystallises in large, orange scales, which, when dried in the air, consist of the hydrated form with an additional molecule of water. The decomposing point is 220—225°. The compound loses all its water at 100°, and the colour changes from orange to ochreous yellow:

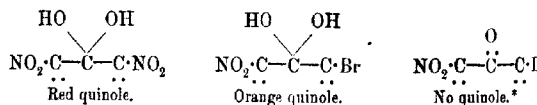
0·1193, dried at 100°, gave 10·7 c.c. N₂ (moist) at 15° and 736·5 mm. N=10·17.

C₉H₁₁O₃N₂Br requires N=10·18 per cent.

0·3363, air-dried, lost 0·0387 at 100°=11·51 H₂O.

C₉H₁₁O₃N₂Br·2H₂O—2H₂O requires a loss=11·58 per cent.

The fact that the bromonitro-compound forms a coloured hydrate like the dinitro-compound, whilst the iodonitro-compound forms no hydrate, is quite in harmony with the quinole structure for the hydrated form (T., 1912, 101, 918), since the existence of this type of structure is dependent upon the central carbon atom being between carbon atoms attached to strongly acid radicles. Thus, the nitro-group and bromine atom are sufficiently acid, whilst the iodine atom is not:



From these results it may be predicted that the chloronitro-compound would form a hydrate redder in colour than the bromo-nitro-compound. We hope to be able to submit this prediction

The nitro-groups in the above formulæ are represented as normal and not as "act" for the sake of simplicity.

to experimental proof on some future occasion, although, as already stated, the isolation of the chloronitroquinone-ammonium derivative has hitherto been found impracticable. The methylation of 2-chloro-6-nitro-4-aminophenol (D.R.-P. 147060; A., 1904, i, 311) should yield the required compound.

Dihaloid Derivatives.

The synthesis of the dinitroquinone-ammonium derivatives by the nitration of the unsubstituted parent compounds (T., 1912, 101, 915) indicated the possibility of directly introducing halogen atoms into the nucleus by a similar process. Some such method was rendered necessary by the fact, already mentioned, that the haloid (chloro- and bromo-) derivatives were too soluble in water to enable them to be conveniently separated from the inorganic salts present in the solution when using the ordinary (Sandmeyer) method of decomposing the diazonium salts. Gattermann's modification of the diazo-reaction would most probably enable these compounds to be prepared by this method, and we propose making experiments in this direction. In the meantime we have succeeded in preparing the dibromo-derivative by direct bromination, as described below.

2:6-Dibromo-4-trimethylammonium-1-benzoquinone.

p-Aminophenol was methylated by methyl iodide and potassium hydroxide in methyl-alcoholic solution, according to the method of Griess, and the iodide, after purification by crystallisation from water, converted into the nitrate by decomposition with silver nitrate. The aqueous solution of the nitrate was used for bromination. On adding an acetic acid solution of bromine to the solution of the nitrate, a dense, crystalline, ochreous precipitate is formed, and the bromine solution is added with constant stirring as long as a turbidity appears on mixing the solutions. The ochreous precipitate consists no doubt of the perbromide of the

dibromo-derivative, $C_6H_2Br_2 \begin{smallmatrix} \text{OH} \\ \diagup \\ N(CH_3)_3 \end{smallmatrix} Br_2$. It was not found possible, however, to isolate this compound, as it is unstable and decomposes with the evolution of bromine on exposure to the air. The washed product was therefore decomposed by aqueous ammonia, in which it dissolved with copious evolution of nitrogen, and the solution, on acidification with hydrochloric acid, slowly deposited dense, colourless prisms of the chloride of the ammonium compound. Numerous analyses of various preparations at this stage proved that the salt had the required formula, but it was difficult to obtain concordant results owing to the retention of two

molecules of water of crystallisation and the tendency to partial efflorescence on drying. A purer salt was afterwards prepared directly from the base, the latter being obtained from the crude chloride by dissolving the salt in water, agitating the hot solution with excess of moist silver oxide, filtering, and evaporating the solution to the crystallising point. The base separated out on cooling in colourless, fern-like leaflets, which retained water at the atmospheric temperature, but which lost water and fell to an opaque, white powder on drying at $110-115^{\circ}$. The compound decomposes at about 207° . The loss of water at 100° was not quite complete, but indicated the retention of three molecules (loss = 13.97 instead of 14.88 per cent.). The substance, when dried at $110-115^{\circ}$, gave the following results:

0.1836 gave 7.35 c.c. N_2 (moist) at 21° and 764.6 mm. $N = 4.58$.

0.2473 „ 0.3020 AgBr (method of Carius). $Br = 51.96$.

$C_9H_{11}ONBr_2$ requires $N = 4.53$; $Br = 51.75$ per cent.

A specimen of the chloride, prepared from the base by dissolving the latter in hot water, adding hydrochloric acid and allowing to crystallise, consisted of long, transparent, colourless prisms, which began to char at about 200° and decomposed at $220-224^{\circ}$:

0.5824 (air-dried) lost 0.0556 at 100° , the crystals becoming opaque without losing their form, and having a decomposing point of $227-228^{\circ}$: The loss, $H_2O = 9.54$ per cent.

0.2213 (oven-dried) gave 7.9 c.c. N_2 (moist) at 17° and 761.6 mm. $N = 4.15$.

0.2696 (oven-dried), decomposed in aqueous solution with silver nitrate, gave 0.1137 AgCl. $Cl = 10.42$.

$C_9H_{12}ONClBr_2$ requires $N = 4.05$; $Cl = 10.26$ per cent.

The loss, $C_9H_{12}ONClBr_2 \cdot 2H_2O - 2H_2O = 9.44$ per cent.

The *picrate* was prepared by mixing a hot aqueous solution of the base with the calculated quantity of picric acid dissolved in hot water. The salt crystallises out on cooling in transparent, yellow scales, decomposing from 198° to 208° . It is but sparingly soluble in alcohol, and crystallises from this solvent in rosettes of yellow, stumpy prisms or serrated leaflets, both forms melting and decomposing at $206-207^{\circ}$:

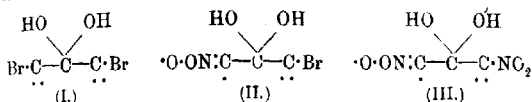
0.1032 gave 9.3 c.c. N_2 (moist) at 19° and 766.3 mm. $N = 10.45$.

$C_9H_{11}ONBr_2 \cdot C_6H_3O_7N_3$ requires $N = 10.41$ per cent.

It was not found possible to determine the bromine in the *picrate* by the method of Carius owing to the explosion of the tube on heating.

Although the constitution of this dibromo-derivative so far as concerns the position of the bromine atoms has not been proved

directly, its mode of formation and its general agreement in all characters with the nitro-haloid and di-iodo-derivatives of known constitution leave no doubt that the bromine atoms are in the positions 2:6. The dependence of colour upon the presence of the nitro-group is strikingly brought out in this case by the colourless hydrated (quinole) and anhydrous (quinonoid) forms. If, as may reasonably be assumed, one of the three molecules of water retained by the base is of the same function as the water of hydration in the dinitro-derivative, it appears that the two bromine atoms are sufficiently acid in character to enable the central carbon atom to retain the two hydroxyls:



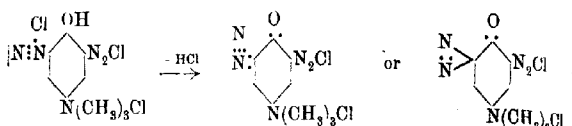
The forms II and III, which represent coloured compounds, cannot be assumed by I. By the benzoylation of the dibromo-compound with benzoyl chloride and sodium hydroxide a product was obtained, the nature of which has not yet been fully made out, and the research requires extension also in this direction.

2: 6-Di-iodo-4-trimethylammonium-1-benzoquinone.

This compound could not be conveniently prepared from the corresponding iodonitro-derivative by reduction and diazotisation of the iodoamino-base, because of the tendency of the reducing agents to remove the iodine atom. It was found unnecessary, however, to pursue this method further, as it was subsequently discovered that the diamino-derivative (T., 1912, 101, 929) could readily be diazotised at both amino-groups with the formation of definite bisdiazonium salts. This property of the diaminotrimethylammonium-benzoquinone compounds is noteworthy in view of the fact that the amino-groups are in the meta-position. It is well known in diazo-chemistry that meta-diamines containing unprotected ortho- or para-positions can only be diazotised at a very low temperature in the presence of a great excess of acid. Even under these conditions the diazotisation is very imperfect so far as concerns one of the amino-groups, owing to the tendency of the diazonium salt to couple with a molecule of the undiazotised base with the formation of the aminoazo-derivative. In the present case the meta-amino-character of the molecule is completely modified by the presence of the trimethylammonium group.

In order to prepare the above compound, the dinitro-trimethylammonium derivative was completely reduced by tin and hydro-

chloric acid, the tin removed as sulphide, and the solution of the chloride, after concentration, diazotised in the usual way. The bisdiazonium salt in solution was decomposed by mixing with an excess of potassium iodide in aqueous solution and boiling as long as nitrogen was evolved. It is of interest to note that the solution of the chloride, which is at first colourless, becomes distinctly orange on diazotisation. It is most probable that the compound which is present in the solution is not simply the bisdiazonium salt, but an anhydride with one of the diazo-groups in the diazo-oxide (quinonediazide) form:



The addition of a concentrated solution of sodium dichromate to the diazotised solution causes the separation of a beautifully crystalline chromate (Meldola and Eynon, T., 1905, **87**, 1), but we have not yet ventured to investigate this compound on account of its violently explosive character.

The crude di-iodo-compound, prepared as above, was purified by crystallisation from hot water, with the addition of silver oxide in order to ensure the decomposition of any salt of the quinone-ammonium base contained in the solution. The substance separate on cooling in beautiful, silvery scales, which become opaque and fall to a crystalline powder on drying in the water-oven. The melting point of the dry compound is 189—190°:

0.2880 (oven-dried) gave 8.3 c.c. N_2 (moist) at 16.7° and 767.7 mm. $\text{N}=3.38$.

0.1985 (oven-dried) gave (by the method of Carius) 0.2312 AgI. $\text{I}=62.92$.

$\text{C}_9\text{H}_{11}\text{ONI}_2$ requires $\text{N}=3.47$; $\text{I}=62.98$ per cent.

The air-dried compound, like the corresponding dibromo-compound, contains 3 molecules of water, one of which is presumably of the same (quinole) function as the water of hydration of the dinitro- and bromonitro-compounds:

0.5091 (air-dried) lost, at 100°, 0.0596 = 11.70 H_2O .

$\text{C}_9\text{H}_{11}\text{ONI}_2 \cdot 3\text{H}_2\text{O} - 3\text{H}_2\text{O}$ requires a loss = 11.82 per cent.

The base dissolves in hydrochloric acid with the formation of a chloride, but this salt was dissociable by water, and could not be isolated. Nitric acid displaces the iodine atoms, and, if sufficiently concentrated, reproduces the original dinitro-compound. The picrate was prepared from the base and picric acid in aqueous

solution, and purified by crystallisation from alcohol. It consists of small, opaque, yellow needles, melting with decomposition at 193–194°:

0.1378 gave 10.4 c.c. N_2 (moist) at 15.5° and 759.6 mm. $N=8.81$.

$C_6H_{11}ONl_2 \cdot C_6H_5O_7N_3$ requires $N=8.92$ per cent.

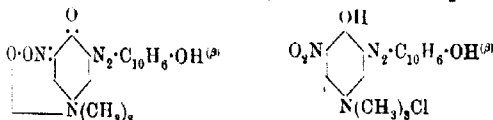
It will be observed that this di-iodo-derivative in both hydrated and anhydrous forms is also a colourless substance.

Nitroazo-derivatives.

Dinitrotrimethylammonium-benzoquinone was reduced by ammonium sulphide, and the solution of the chloride of the nitro-amino-base, obtained in the way previously described, was diazotised by the usual method. The solution of the diazonium salt, on mixing with an alkaline solution of β -naphthol, gave an immediate precipitate of a deep violet azo-compound. The latter was collected, washed, and dried. It was noticed that the deep violet colour of the freshly precipitated and semi-gelatinous azo-compound immediately changed to a bright scarlet on contact with hydrochloric acid, the violet colour being gradually restored on washing with water, and immediately on contact with alkali. From these remarkable colour changes, it was concluded that the quinonoid benzene nucleus still retained its basic character, notwithstanding the attachment of the azo-naphthol group. This conclusion was subsequently verified by the isolation of the chloride.

The azo-compound is sufficiently basic to dissolve in glacial acetic acid, but the acetate is dissociable by water. Advantage of this property was taken therefore in order to purify the substance, which was dissolved in hot glacial acetic acid; the solution, which was of an orange-red colour, was filtered, and then freely diluted with hot water. The azo-compound separated from the solution on cooling in small rosettes of bronzy needles. The latter were collected, washed with alcohol, and dried in the water-oven. Analysis indicated that the compound was the nitro-azo-derivative:

6-Nitro-2- β -naphtholazo-4-trimethylammonium-1-benzoquinone.



0.0944 gave 0.2148 CO_2 and 0.0412 H_2O . $C=62.06$; $H=4.84$.

0.0628 „ 8.2 c.c. N_2 (moist) at 16° and 771.4 mm. $N=15.45$.

$C_{18}H_{18}O_4N_4$ requires $C=62.26$; $H=4.95$; $N=15.34$ per cent.

The azo-compound melts and decomposes above 300°. It is but

very sparingly soluble in boiling alcohol, and imparts a beautiful violet colour to this solvent. It is non-phenolic in character, but dissolves in alcoholic sodium hydroxide with a violet colour, the solution becoming red and depositing scarlet crystals of the chloride on the addition of hydrochloric acid. The compound dissolves in concentrated sulphuric acid with a violet colour, which becomes red on dilution; it dissolves also in hot aniline with a bluish-violet colour. An air-dried specimen of the azo-compound underwent a loss on drying at 100° , indicating that the hydrated form is in this case also capable of existence, the loss in weight corresponding with rather more than that required for one molecule of water:

0.2492 lost 0.0148 = 5.94.

$C_{19}H_{18}O_4N_4 \cdot H_2O - H_2O$ requires a loss = 4.7 per cent.

The hydrated crystals fall to a bronzy, crystalline powder, but otherwise undergo no great change in appearance.

The *chloride* (formulated above) was prepared by adding excess of hydrochloric acid to the hot solution of the azo-compound in glacial acetic acid, and allowing the salt to crystallise out. It consists of brick-red needles, which can be safely washed with alcohol and dried in the water-oven without undergoing dissociation:

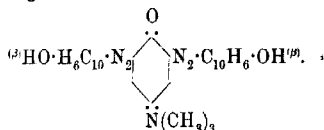
0.1254 gave 14.4 c.c. N_2 (moist) at 15.5° and 763.1 mm. $N = 13.47$.

0.2970 „ 0.1034 AgCl. $Cl = 8.61$.

$C_{19}H_{18}O_4N_4Cl$ requires $N = 13.91$; $Cl = 8.80$ per cent.

(The chlorine was determined by decomposing the salt with warm, dilute ammonia, collecting the free azo-compound, and precipitating the silver chloride from the filtrate acidified with nitric acid in the usual way.)

Of the diazo-compounds belonging to this series we have prepared the type containing the two azonaphthol groups:



This and analogous compounds will be made the subjects of further investigation.

We desire to express our thanks to Mr. Robert O. Bishop, who has rendered us valuable assistance in connexion with the analytical part of the work.

CITY AND GUILDS OF LONDON INSTITUTE,
FINSBURY TECHNICAL COLLEGE.

XXIII.—The Constituents of the Rhizome and Roots of *Caulophyllum thalictroides*.

By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

Caulophyllum thalictroides (Linné), Michaux (Nat. Ord., *Berberidaceæ*), commonly known, among other names, as "Blue Cohosh," is a plant indigenous to North America, and is the only known species of the genus. Although the rhizome and roots of this plant, or preparations therefrom, are considerably employed in medicine, the drug is not at present recognised by any of the national Pharmacopœias.

Caulophyllum appears to have been first chemically examined by F. F. Mayer (*Amer. J. Pharm.*, 1863, **35**, 99), who stated it to contain a saponaceous principle and a colourless alkaloid, although the latter was not actually isolated. A. E. Ebert (*ibid.*, 1864, **36**, 203) also observed the presence of a substance analogous to saponin, but failed to obtain an alkaloid. It was, however, definitely shown by J. U. Lloyd ("Drugs and Medicines of North America," Vol. II., 1887, p. 153, and *Proc. Amer. Pharm. Assoc.*, 1893, **41**, 115) that caulophyllum contains an appreciable amount of an alkaloid, which he designated "caulophylline," but its composition was not determined. Although he did not succeed in crystallising the base, the hydrochloride was described as forming acicular crystals. The present authors have obtained the respective alkaloid in a pure, crystalline state, and have proved it to be methylecystisine.

A saponin-like substance was also isolated from caulophyllum by Lloyd (*loc. cit.*, 1887, p. 151), who was the first to obtain it in a crystalline and apparently pure state, and found it to be a glucoside. This compound, the general properties of which were described, was termed "leontin," with reference to an old botanical name (*Leontice*) of the plant. Several analyses of the substance, conducted by H. Trimble, led the latter to assign to it the formula $C_{18}H_{26}O_8 \cdot H_2O$. Although from the results of the present investigation the percentage composition of the compound appears to have been accurately determined, thus affording evidence of its purity, yet the formula deduced therefrom is incorrect. A consideration of the products of hydrolysis, which have now for the first time been determined, has shown the compound to be represented by the formula $C_{54}H_{88}O_{17} \cdot 4H_2O$, and it is proposed to designate it *caulosaponin*. It has, furthermore, been shown that caulophyllum contains a second saponin-like glucoside, which, although present in much smaller proportion than that above mentioned, has also been obtained in a crystalline state and completely characterised. It

possesses the formula $C_{66}H_{104}O_{17}$, and has been termed *caulophyllosaponin*.

Gilbard (*Analyst*, 1911, 36, 270) has suggested a test for the identification of the so-called "caulophyllin," an impure resinous product obtained from caulophyllum, which is used to some extent medicinally. The colour reaction upon which this test depends is due to the presence of the above-mentioned glucosides.

A summary of the substances isolated in the present investigation, and their derivatives, together with some physiological tests, is given at the end of this paper.

EXPERIMENTAL.

The material employed for this investigation consisted of the rhizome and roots of *Caulophyllum thalictroides* (Linné), Michaux. It was perfectly authentic, having been specially gathered in North Carolina, and kindly supplied to us by Professor J. U. Lloyd, of Cincinnati, Ohio, to whom our best thanks may here be expressed.

A small portion (10 grams) of the material was first tested for the presence of an alkaloid, and with a positive result.

In order to ascertain whether an enzyme were present, 100 grams of the ground material were macerated with water at the ordinary temperature for two days. To the expressed and filtered liquid about twice its volume of alcohol was added, when a gelatinous precipitate was produced. This was collected, washed with a little alcohol, and dried in a vacuum over sulphuric acid, when it amounted to 0.3 gram. It gave the biuret reaction, and slowly hydrolysed amygdalin, thus proving the presence of an enzyme.

Another portion (25 grams) of the ground material was completely extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100° , were obtained:

Petroleum (b. p. $35-50^{\circ}$)	extracted	0.15 gram	=	0.60 per cent.
Ether	"	0.65 "	=	2.60 "
Chloroform	"	0.81 "	=	3.24 "
Ethyl acetate	"	0.42 "	=	1.68 "
Alcohol	"	4.90 "	=	19.60 "

Total 6.93 grams = 27.72 per cent.

For the purpose of a complete examination, 22.37 kilograms of the ground material were completely extracted with hot alcohol, when, after the removal of the greater portion of the alcohol, 8.28 kilograms of a dark-coloured, viscid extract were obtained.

Two kilograms of the above-mentioned extract were mixed with water, and the mixture distilled in a current of steam. The distillate was extracted with ether, and the solvent removed, when

about 1 gram of a pale yellow essential oil was obtained. This had a pleasant odour, and yielded the colour reaction for furfuraldehyde.

After the above operation there remained in the distillation flask a dark-coloured aqueous liquid (A), which contained in suspension a considerable quantity of grey, amorphous material (B), and, on cooling, the whole formed a soft, gelatinous mass. The separation of the amorphous material from the aqueous liquid was effected by agitating the mixture with hot amyl alcohol, which dissolved all the solid substance, with the exception of a very small amount of indefinite material which was removed by filtration. The amyl alcohol extract was subsequently washed with water, the washings being added to the main portion of the aqueous liquid.

Examination of the Aqueous Liquid (A).

The aqueous liquid, which had been treated with amyl alcohol as above described, was next extracted many times with ether. The ethereal liquids were united, washed, dried, and the solvent removed, when 2 grams of a viscid, brown residue were obtained. This was agitated with alcohol, when a sparingly soluble solid separated, which, when crystallised from a mixture of pyridine and alcohol, was obtained in colourless leaflets, melting and decomposing at $275-280^{\circ}$. The substance yielded an acetyl derivative melting at 169° , which, together with its colour reactions, indicated it to be citrullol, $C_{23}H_{45}O_2(OH)_2$. It was subsequently obtained in larger amount from an ethereal extract of the above-mentioned grey, amorphous material, and was then completely identified.

The aqueous liquid, after extraction with ether as above described, frothed strongly on agitation, and evidently contained some saponin-like substance which had not been removed by the previous treatment with amyl alcohol. With the object of effecting the complete removal of this substance, the aqueous liquid was again shaken repeatedly with hot amyl alcohol, these extracts being then united, washed with a little water, and the solvent removed by distillation under diminished pressure. A quantity (25 grams) of a dark brown solid was thus obtained, which was glucosidic, and possessed the characters of a saponin. It was dissolved in alcohol, and the solution kept for some time, when a colourless, crystalline substance separated, which, after recrystallisation from alcohol, melted and decomposed at $250-255^{\circ}$. This compound was found to be identical with a glucoside which was obtained in larger amount from the amorphous material extracted by the first treatment of the aqueous liquid with amyl alcohol, and has been designated *caulosaponin*. It is fully described in connection with the examination of the grey, amorphous product (B).

The aqueous liquid was next treated with a slight excess of basic lead acetate, which produced a relatively small amount of a dark brown precipitate. This was collected, washed, suspended in water, and decomposed by hydrogen sulphide, but no definite substance could be isolated from it. The filtrate from the basic lead acetate precipitate was deprived of lead by means of hydrogen sulphide, and the clear, filtered liquid concentrated under diminished pressure to a convenient volume. It then readily responded to the tests for an alkaloid, and was also found to contain a quantity of reducing sugar. From a small portion of the liquid, *d*-phenylglucosazone (m. p. 210°) was prepared.

Isolation of Methylcystisine, $C_{11}H_{15}ON_2(CH_3)$.

In order to isolate the alkaloid from the above-mentioned aqueous liquid, the entire remaining portion of the latter was made alkaline with sodium hydroxide and repeatedly extracted with chloroform. The chloroform extracts were united, washed with a little water, dried, and the solvent removed, when about two grams of a viscid, brown residue were obtained, which gave the reactions for an alkaloid. For the purpose of purifying this material, it was dissolved in dry chloroform, and a current of dry hydrogen chloride passed into the solution, when a colourless hydrochloride of the base was precipitated. This was collected, and crystallised from a mixture of alcohol and ethyl acetate, when it separated in colourless prisms, decomposing at 250 – 255° . The air-dried substance was analysed with the following results:

0.0967 gave 0.1726 CO_2 and 0.0594 H_2O . C=48.7; H=6.8.

0.1212 „ 10.3 c.c. N_2 at 20° and 757 mm. N=9.7.

0.1105 „ 0.1078 AgCl. Cl=24.1.

$C_{12}H_{18}ON_2Cl_2 \cdot H_2O$ * requires C=48.8; H=6.8; N=9.5;

Cl=24.1 per cent.

In order to obtain the free base, the hydrochloride was dissolved in a little water, the solution made alkaline with sodium hydroxide, and then extracted six times with chloroform. The united chloroform extracts were washed with a very small quantity of water, then dried, and the solvent removed. The residue, which soon solidified, was recrystallised from a mixture of benzene and light petroleum, when the base was obtained in colourless, prismatic needles, melting at 137° . For the purpose of its complete examination, the entire remaining portion of the original alcoholic extract of the drug was worked up in the manner already described. The

* The water of crystallisation in this salt could not be directly determined, since the substance slowly loses hydrogen chloride on dehydration.

RHIZOME AND ROOTS OF CAULOPHYLLUM THALICTROIDES. 195

total amount of pure alkaloid thus obtained, calculated as the free base, was about 5 grams. It was analysed, and its molecular weight determined, with the following results:

0.1076 gave 0.2794 CO₂ and 0.0780 H₂O. C=70.8; H=8.0.

0.1122 „ 13.4 c.c. N₂ at 21° and 762 mm. N=13.6.

0.4666, in 27.23 benzene, gave Δt=0.387°. M.W.=221.

C₁₃H₁₆ON₂ requires C=70.6; H=7.8; N=13.7 per cent. M.W.=204.

The alkaloid was optically active, and a determination of its specific rotatory power gave the following result:

0.2256, made up to 20 c.c. with water, gave α_D -5.0° in a 2-dm. tube, whence [α]_D -221.6°.

A small amount of the alkaloid was dissolved in a known volume of N/10-sulphuric acid, and the excess of the latter titrated with N/10-barium hydroxide, using iodococin as indicator in the presence of ether.

0.1305 neutralised 6.4 c.c. N/10-H₂SO₄, which is the theoretical amount required for C₁₂H₁₆ON₂ as a monacidic base.

The alkaloid was readily soluble in water, alcohol, chloroform, or benzene, but less readily in ether. The aurichloride was obtained in golden-yellow needles, which decomposed at 205°.

0.1550 gave 0.1512 CO₂, 0.0443 H₂O, and 0.0561 Au. C=26.6; H=3.2; Au=36.2.

C₁₂H₁₇ON₂.AuCl₄ requires C=26.5; H=3.1; Au=36.2 per cent.

The composition of the above-described alkaloid and its salts, together with its general characters, indicated it to be methylcytisine. This compound had not hitherto been known to occur in nature, although it has previously been prepared by the methylation of cytisine, C₁₁H₁₄ON₂, an alkaloid found in the common laburnum (*Cytisus Laburnum*, Linné) and other species of *Cytisus*, as well as in various other plants. It represents the alkaloid previously obtained by J. U. Lloyd (*Proc. Amer. Pharm. Assoc.*, 1893, **41**, 115), and designated by him "caulophylline," as its composition had not then been determined. Methylcytisine *picrate* appears not to have previously been prepared. This salt crystallised from hot water in long, yellow needles, which sintered at about 200°, and melted completely at 228°.

Although the characters of the above-described alkaloid were in quite complete agreement with those of methylcytisine, as recorded in the literature (compare Buchka and Magalhães, *Ber.*, 1891, **24**, 678; Partheil, *Arch. Pharm.*, 1892, **230**, 448; and Rauwerda, *ibid.*, 1900, **238**, 484), a small amount of the latter compound was pre-

* The melting point of 245°, as given by Buchka and Magalhães (*loc. cit.*), for methylcytisine, is obviously an error.

pared from a commercial specimen of cytisine for the purpose of comparison. It melted at 135° , and when mixed with the alkaloid from caulophyllum no depression of the melting point ensued. The identification of the last-mentioned alkaloid as methylcytisine was thus completely effected.

Quantitative Determination of the Alkaloid in Caulophyllum.—

Having determined the composition and characters of the alkaloid in caulophyllum, it seemed desirable to formulate a method for ascertaining the proportion in which it exists in the drug. The following method of procedure was found to give satisfactory results:

Twenty grams of caulophyllum, in No. 60 powder, were introduced into a suitable flask, 100 c.c. of chloroform and 10 c.c. of aqueous sodium carbonate (10 per cent. solution) added, and the whole was vigorously shaken from time to time during a period of four hours. The mixture was then filtered, and 50 c.c. of the chloroform liquid (=10 grams of caulophyllum) transferred to a separator, in which it was vigorously shaken with 10 c.c. of $N/10$ -sulphuric acid. After separating the acid liquid from the chloroform, the latter was again shaken with 10 c.c. of $N/10$ -sulphuric acid. The two portions of acid liquid were united, extracted with 20 c.c. of ether, which removed a small quantity of emulsified chloroform, then made alkaline by the addition of 5 c.c. of aqueous sodium carbonate (10 per cent. solution), and agitated with three successive portions of chloroform of 20 c.c. each. The united chloroform extracts were washed twice with water, using each time 2 c.c. of the latter, and the chloroform then carefully removed by distillation. The residual alkaloid was dissolved in 10 c.c. of $N/50$ -sulphuric acid, 10 c.c. of ether added, the solution transferred to a stoppered bottle, and the excess of sulphuric acid determined by titration with $N/50$ -barium hydroxide, using iodoeosin as the indicator. It was thus found that 2.1 c.c. $N/50$ -sulphuric acid were required to neutralise the alkaloid, and as it has already been shown that methylcytisine, $C_{12}H_{16}ON_2$, under the above conditions of titration, possesses the character of a monacidic base, the corresponding amount of alkaloid would be 2.1×0.00408 or 0.0086 gram. This is equivalent to 0.086 per cent. of methylcytisine in the drug.

In a second assay of the caulophyllum, the digestion with chloroform and aqueous sodium carbonate was prolonged for twenty hours, but the process was otherwise conducted as before. The amount of alkaloid thus obtained was equivalent to 0.078 per cent. of the drug, and the two determinations may therefore be considered to agree within the limits of experimental error. From this result it was also apparent that the digestion of the drug for a period of more than four hours presents no advantage.

The accuracy of the above-described method for the quantitative determination of the alkaloid was controlled by dissolving 0.0098 gram of pure methylcytisine in 50 c.c. of chloroform, and treating this solution in precisely the same manner as the chloroform extract of the drug. The amount of alkaloid indicated by the final titration was 0.0096 gram.

Examination of the Grey, Amorphous Material (B).

As previously noted, the aqueous liquid remaining after the distillation of the original alcoholic extract with steam contained a quantity of grey, amorphous material in suspension, which was removed by extraction with hot amyl alcohol. This amyl alcohol solution was concentrated to a small bulk under diminished pressure, and a large volume of ether added, which precipitated a greyish-white solid.

Isolation of a Crystalline Glucoside, Caulosaponin, $C_{54}H_{88}O_{17} \cdot 4H_2O$.

The above-mentioned greyish-white solid was collected, and amounted to 94 grams. It was dissolved in hot alcohol, and the solution kept for some time, when a crystalline, glucosidic substance was deposited. This was crystallised several times from alcohol, and was finally obtained in colourless, slender needles, melting and decomposing at 250–255°. The amount of pure substance isolated from 2 kilograms of the original alcoholic extract was 16 grams. For the purpose of its complete examination, a further and larger quantity was subsequently obtained by working up the remainder of the alcoholic extract in the manner already described:

0.1173, when heated at 115°, lost 0.0077 H_2O . $H_2O = 6.6$.

0.1017 * gave 0.2394 CO_2 and 0.0796 H_2O . $C = 64.2$; $H = 8.7$.

0.1074 * „ 0.2520 CO_2 „ 0.0836 H_2O . $C = 64.0$; $H = 8.6$.

$C_{54}H_{88}O_{17} \cdot 4H_2O$ requires $H_2O = 6.7$ per cent.

$C_{54}H_{88}O_{17}$ requires $C = 64.3$; $H = 8.7$ „ „

A comparison of the composition and properties of this compound with those of the glucoside previously isolated by J. U. Lloyd, and described by him under the name of "leontin" (*Drugs and Medicines of North America*, Vol. II., 1887, p. 151), renders it evident that the substances are identical. In view of the fact, however, that the compound has now been completely characterised, and that, by an examination of its hydrolytic products, it has been shown to possess the formula $C_{54}H_{88}O_{17} \cdot 4H_2O$, instead of $C_{16}H_{26}O_5 \cdot H_2O$, as originally assigned to it (*loc. cit.*), it is deemed desirable to give it the new and distinctive name of *caulosaponin*. This is the more

* Anhydrous substance.

important as the name "leontin" appears also to have been given to a preparation of caulophyllum which does not represent the pure glucoside.

Caulosaponin, $C_{54}H_{88}O_{17} \cdot 4H_2O$, is insoluble in water, ether, chloroform, or benzene, but is moderately soluble in hot alcohol, although sparingly so in cold. It possesses phenolic properties, and dissolves readily in solutions of the alkali hydroxides. When the substance is dissolved in acetic anhydride, a little chloroform added, and subsequently a few drops of concentrated sulphuric acid, a purplish-red coloration is produced, which gradually fades. A solution of caulosaponin in water containing a little alcohol yields, on agitation, an abundant and persistent froth, and the substance is therefore a member of that class of compounds which have been designated as saponins. So far as known to us, only one other well-characterised substance of this class has previously been obtained in a crystalline form (compare *Arch. Pharm.*, 1912, 250, 427).

Deca-acetylaulosaponin, $C_{54}H_{76}O_{17}(CO \cdot CH_3)_{10}$.—This derivative of caulosaponin was prepared by heating the latter with acetic anhydride for two hours. The mixture was then poured into water, and the precipitated solid collected, washed, and dried in a vacuum desiccator over sulphuric acid and solid potassium hydroxide. The product was thus obtained as a white powder, which melted at $135\text{--}140^\circ$. It was readily soluble in the usual organic solvents, but could not be crystallised:

0.1323 gave 0.3017 CO_2 and 0.0899 H_2O . $C=62.2$; $H=7.6$.

$C_{74}H_{108}O_{27}$ requires $C=62.2$; $H=7.6$ per cent.

It is thus evident that caulosaponin contains ten hydroxyl groups.

Hydrolysis of Caulosaponin.

Formation of Caulosapogenin, $C_{42}H_{62}O_2(OH)_4$, and Dextrose.

Twenty grams of caulosaponin were dissolved in 500 c.c. of alcohol, then 150 c.c. of a 10 per cent. aqueous solution of hydrogen chloride added, and the mixture heated on a water-bath for several hours, when a crystalline hydrolytic product separated from the hot liquid. After removal of the alcohol in a current of steam, the mixture was filtered, the filtrate being set aside for the subsequent examination of the sugar. The crystalline product was well washed with water, and purified by recrystallisation from dilute pyridine. It was thus obtained in colourless, anhydrous, rhombohedral prisms, which decomposed at about 315° :

0.0893 gave 0.2474 CO_2 and 0.0806 H_2O . $C=75.6$; $H=10.0$.

0.0791 " 0.2195 CO_2 " 0.0716 H_2O . $C=75.7$; $H=10.1$.

$(C_7H_{11}O)_x$ requires $C=75.7$; $H=9.9$ per cent.

The molecular weight of the above-described compound could not be directly determined on account of its sparing solubility in suitable solvents. An examination of its derivatives showed, however, that it possesses the formula $C_{42}H_{66}O_6$, and that it contains four hydroxyl groups, one of which is phenolic. As it is a new compound, it is proposed to designate it *caulosapogenin*.

Caulosapogenin, $C_{42}H_{66}O_6(OH)_4$, is insoluble in water, chloroform, or benzene, and sparingly soluble in absolute alcohol, but more readily so in alcohol containing a little water. It also dissolves in aqueous alkali hydroxides in the presence of alcohol, and is therefore phenolic in character. When caulosapogenin is dissolved in acetic anhydride, a little chloroform added, and subsequently a few drops of concentrated sulphuric acid, a rose-red coloration is produced which gradually disappears. When a solution of the substance in aqueous alcohol is agitated, a copious frothing is produced, but the permanency of the latter is not so great as in the case of the glucoside itself.

Tetra-acetylcaulosapogenin, $C_{42}H_{62}O_6(CO \cdot CH_3)_4$.—This compound was prepared by heating caulosapogenin for some time with acetic anhydride, the solution being then concentrated and poured into water. The product, which soon solidified, was collected, washed well with water, and dried over sulphuric acid and solid potassium hydroxide, when it formed a white, amorphous powder, which melted at 120° . It was extremely soluble in the usual organic solvents, but could not be crystallised:

0.1040 gave 0.2743 CO_2 and 0.0866 H_2O . $C=71.9$; $H=9.2$.

$C_{50}H_{74}O_{10}$ requires $C=71.9$; $H=8.9$ per cent.

Diacetylcaulosapogenin, $C_{42}H_{64}O_6(CO \cdot CH_3)_2$.—The above-described tetra-acetyl derivative, when heated with ammonium carbonate in the presence of alcohol, readily loses two acetyl groups. The resulting diacetyl compound crystallises from dilute alcohol in thin, colourless needles, which melt at $160-162^\circ$:

0.1221 gave 0.3288 CO_2 and 0.1036 H_2O . $C=73.4$; $H=9.4$.

$C_{46}H_{70}O_8$ requires $C=73.6$; $H=9.3$ per cent.

Diacetylcaulosapogenin possesses phenolic properties, and yields a crystalline sodium derivative.

Diacetylmonosodiocaulosapogenin, $C_{42}H_{63}O_6Na(CO \cdot CH_3)_2$.—This compound is best prepared by agitating an ethereal solution of tetra-acetyl- or diacetyl-caulosapogenin with aqueous sodium carbonate, when the sodium derivative separates in colourless needles:

0.1818, when heated at 115° , lost 0.0094 H_2O . $H_2O=5.2$.

0.1488* gave 0.0138 Na_2SO_4 . $Na=3.0$.

$C_{46}H_{69}O_6Na \cdot 2H_2O$ requires $H_2O=4.5$ per cent.

$C_{46}H_{69}O_6Na$ requires $Na=3.0$ per cent.

* Anhydrous substance.

The number of acetyl groups in this sodium derivative was directly determined by heating the substance with a known volume of *N*/10-alcoholic sodium hydroxide, and titrating the excess of alkali with standard acid:

0.3191 gave on hydrolysis acetic acid equivalent to 8.45 c.c. *N*/10-NaOH. $\text{CO}\cdot\text{CH}_3 = 11.4$.

$\text{C}_{42}\text{H}_{88}\text{O}_6\text{Na}(\text{CO}\cdot\text{CH}_3)_2$ requires $\text{CO}\cdot\text{CH}_3 = 11.1$ per cent.

Tetra benzoylcaulosapogenin, $\text{C}_{42}\text{H}_{62}\text{O}_8(\text{CO}\cdot\text{C}_6\text{H}_5)_4$.—This compound was prepared by heating caulosapogenin in pyridine solution with benzoyl chloride for about an hour. The mixture was then poured into water, rendered slightly alkaline with sodium carbonate, and kept for some time, when the reaction product slowly solidified. It was collected and purified by crystallisation from a mixture of chloroform and alcohol, when the substance separated in well-formed, hexagonal prisms, melting at 288° . An analysis and a determination of its molecular weight gave the following results:

0.1040 gave 0.2946 CO_2 and 0.0735 H_2O . $\text{C} = 77.3$; $\text{H} = 7.9$.

0.5529 in 25.2 benzene gave $\Delta t = 0.102^\circ$. $\text{M.W.} = 1076$.

$\text{C}_{70}\text{H}_{82}\text{O}_{10}$ requires $\text{C} = 77.6$; $\text{H} = 7.6$ per cent. $\text{M.W.} = 1082$.

The preceding results have thus served to establish the correctness of the formula assigned to caulosapogenin.

Tetra benzoylcaulosapogenin is readily soluble in ether, chloroform, or benzene, but only sparingly so in water or alcohol. It does not possess the phenolic properties of the original substance. Its specific rotatory power was determined, with the following result:

0.3092, made up to 20 c.c. with chloroform, gave $\alpha_D + 3.26'$ in a 2-dcm. tube, whence $[\alpha]_D + 111.0^\circ$.

Caulosapogenin Monomethyl Ether, $\text{C}_{42}\text{H}_{68}\text{O}_5(\text{O}\cdot\text{CH}_3)$.—This substance was prepared by heating caulosapogenin for several hours with alcoholic sodium hydroxide and methyl iodide. When crystallised from dilute alcohol, it separated in well-formed needles, melting at 235° :

0.1143 gave 0.3173 CO_2 and 0.1059 H_2O . $\text{C} = 75.7$; $\text{H} = 10.3$.

The number of methoxyl groups in the compound was determined by Perkin's modification of Zeisel's method:

0.1318 gave 0.0544 AgI. $\text{MeO} = 5.5$.

$\text{C}_{42}\text{H}_{68}\text{O}_5(\text{OMe})$ requires $\text{C} = 75.9$; $\text{H} = 10.0$; $\text{MeO} = 4.6$ per cent.

The specific rotatory power of the substance was determined with the following result:

0.1412, made up to 20 c.c. with chloroform, gave $\alpha_D + 1.23'$ in a 2-dcm. tube, whence $[\alpha]_D + 74.4^\circ$.

Oxidation of Caulosapogenin.

With the object of obtaining further information respecting the nature of caulosapogenin, a quantity (10 grams) of the latter was dissolved in aqueous potassium hydroxide with the addition of a little pyridine, and a 4 per cent. solution of potassium permanganate gradually added, the mixture being heated on a water-bath. The oxidation proceeded rapidly at first, but after the addition of about 400 c.c. of the permanganate solution (about 10 atomic proportions of oxygen) the latter was only slowly decolorised. The mixture was then filtered under pressure, and the alkaline liquid extracted with ether, but nothing was thus removed. On subsequently acidifying the liquid, a voluminous precipitate was produced, which was collected, washed with water, and then dissolved in ether. The ethereal liquid, on keeping a short time, deposited a crystalline, acidic substance, which was recrystallised from dilute alcohol. It separated from this solvent in thin, colourless needles, which decomposed at 310° . An analysis and a determination of the molecular weight gave the following results:

0.1096 gave 0.2191 CO_2 and 0.0922 H_2O . $\text{C} = 72.7$; $\text{H} = 9.3$.

0.1606 in 25.75 acetic acid gave $\Delta t = 0.093^{\circ}$. $\text{M.W.} = 261$.

$\text{C}_{16}\text{H}_{24}\text{O}_3$ requires $\text{C} = 72.7$; $\text{H} = 9.1$ per cent. $\text{M.W.} = 264$.

0.1075 neutralised 4.15 c.c. $N/10\text{-NaOH}$.

A monocarboxylic acid, $\text{C}_{16}\text{H}_{24}\text{O}_3$, requires 4.10 c.c. $N/10\text{-NaOH}$.

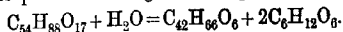
Since the above-described acid, $\text{C}_{16}\text{H}_{24}\text{O}_3$, does not agree in its properties with any acid of this formula which has heretofore been recorded, it is evidently a new compound, but the amount obtained was too small to permit of its further examination. It may, however, be concluded that the oxidation of caulosapogenin with potassium permanganate effects a far-reaching degradation of the molecule.

Examination of the Sugar yielded by the Hydrolysis of Caulosaponin.

The aqueous acid liquid resulting from the hydrolysis of the glucoside caulosaponin, as above described, was exactly neutralised with sodium carbonate, and evaporated to dryness under diminished pressure. The residue was then digested with hot alcohol, the mixture filtered, and the filtrate concentrated, when a viscid syrup was obtained. The latter yielded *d*-phenylglucosazone, which, after crystallisation from dilute pyridine, melted and decomposed at 212° .

The above results have thus shown that caulosaponin is resolved on hydrolysis into caulosapogenin and dextrose. A known quantity of the glucoside, when hydrolysed by dilute hydrochloric acid in

the presence of alcohol, and the alcohol subsequently removed, yielded 64.1 per cent. of its weight of caulosapogenin ($C_{34}H_{88}O_{17}$ requires $C_{42}H_{66}O_6 = 66.1$ per cent.). The hydrolysis of caulosaponin therefore takes place according to the equation:



The amyl-alcoholic liquid, from which the caulosaponin had been separated by treatment with ether, as above described, was brought on to purified sawdust, the mixture thoroughly dried, and then extracted successively in a large Soxhlet apparatus with light petroleum, ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Amorphous Material (B).

This was a dark coloured, fatty product, amounting to 49 grams. It was hydrolysed by heating for a short time with an alcoholic solution of potassium hydroxide, after which the alcohol was removed, water added, and the alkaline mixture extracted with ether. The ethereal liquid was washed, dried, and the solvent removed, when 11 grams of a viscid residue were obtained.

Isolation of a Phytosterol, $C_{27}H_{46}O$.

The above-mentioned residue of unsaponifiable material was digested with cold alcohol, which removed a quantity of gummy matter, leaving a crystalline solid undissolved. The latter was collected, and, after several crystallisations from ethyl acetate, was obtained in colourless leaflets, melting at 153° . The substance gave the colour reaction of the phytosterols, and evidently belonged to that class of compounds:

0.0918* gave 0.2812 CO_2 and 0.1002 H_2O . $C = 83.5$; $H = 12.1$.

$C_{27}H_{46}O$ requires $C = 83.9$; $H = 11.9$ per cent.

Examination of the Fatty Acids.

The aqueous alkaline liquid which had been extracted with ether for the removal of the unsaponifiable material, as above described, was acidified with dilute sulphuric acid, and again extracted with ether. After the removal of the solvent, the residual fatty acids were converted into their lead salts, and the latter treated with ether. The soluble portion, when decomposed by hydrochloric acid, yielded 18 grams of liquid acids, whilst the insoluble portion gave about 5 grams of solid acids.

The Liquid Acids.—These acids were distilled under diminished

* Dried at 110° .

RHIZOME AND ROOTS OF CAULOPHYLLUM THALICTROIDES. 203

pressure, and passed over at 210—245°/15 mm. as a pale yellow oil. An analysis and a determination of the neutralisation and iodine values gave the following results:

0.1176 gave 0.3310 CO₂ and 0.1264 H₂O. C=76.8; H=11.9.

Neutralisation value=199.1; Iodine value=159.

C₁₈H₃₄O₂ requires C=76.6; H=12.1 per cent. N.V.=198.9;
I.V.=90.1.

C₁₈H₃₂O₂ requires C=77.1; H=11.4 per cent. N.V.=200.4;
I.V.=181.4.

It would appear from these results that the liquid acids consisted of a mixture of oleic and linolic acids.

The Solid Acids.—These acids were converted into the methyl ester, and the latter separated by distillation under diminished pressure into two fractions, one of which was collected at 200—205°, and the other above 205°/20 mm. The first fraction yielded, on hydrolysis, a product which melted at 55—56°, and had a neutralisation value of 214; it evidently consisted of a mixture of palmitic and stearic acids. The fraction of ester distilling above 205°/20 mm. gave, on hydrolysis, an acid which separated from hot ethyl acetate in small leaflets, melting at 75—76°, and was identified as cerotic acid (Found, C=78.6; H=13.3. Calc., C=78.8; H=13.1 per cent.).

Ethereal Extract of the Amorphous Material (B).

Isolation of Citrullol, C₂₈H₄₈O₂(OH)₃.

The ethereal extract was a greyish-white powder, and amounted to 71 grams. It was dissolved in hot alcohol, and the solution kept for some time, when a small quantity of a sparingly soluble substance slowly separated. The latter was collected and crystallised from a mixture of pyridine and alcohol, when it was obtained in colourless leaflets, melting and decomposing at about 275—280°. The substance gave the colour reactions of ipuranol and allied alcohols, and yielded an acetyl derivative melting at 169—170°. These properties, together with an analysis of the substance (Found, C=71.9; H=10.4. Calc., C=72.4; H=10.3 per cent.), proved its identity with citrullol, C₂₈H₄₈O₃ (compare T., 1910, **97**, 102; and P., 1912, **28**, 318).

Isolation of a New Crystalline Glucoside, Caulophyllosaponin,



The alcoholic liquid remaining after the separation of the above-described citrullol was heated on a water-bath, and water gradually

added until turbidity ensued, when a crystalline solid separated on cooling. Some difficulty was experienced in purifying this substance, owing to the presence of small quantities of citrullol and caulosaponin, but after a process of fractional crystallisation from dilute alcohol it was obtained in colourless, silky needles, melting and decomposing at 250–260°. The substance was glucosidic and anhydrous. It was analysed, with the following results:

0.1129 gave 0.2803 CO₂ and 0.0916 H₂O. C=67.7; H=9.0.

0.1050 „ 0.2611 CO₂ „ 0.0880 H₂O. C=67.8; H=9.3.

C₆₆H₁₀₄O₁₇ requires C=67.8; H=8.9 per cent.

These results, together with the data subsequently obtained by an examination of the hydrolytic products of the glucoside, showed it to possess the formula C₆₆H₁₀₄O₁₇. As no glucoside of this formula has hitherto been recorded, it is proposed to designate the above-described compound *caulophyllosaponin*, with reference to the source from which it has been obtained, and the fact that it has the properties of a saponin. For its complete examination, the amount obtained from the total (8.28 kilograms) original alcoholic extract of the drug was employed.

Caulophyllosaponin, C₆₆H₁₀₄O₁₇, is extremely soluble in alcohol, sparingly so in ether, and insoluble in water. It dissolves in solutions of the alkali hydroxides, and possesses phenolic properties. A solution of the substance in water containing a little alcohol yields, on agitation, an abundant and persistent froth. When the substance is dissolved in acetic anhydride, a little chloroform added, and subsequently a few drops of concentrated sulphuric acid, a purplish-red colour is produced, quite analogous to that yielded under the same conditions by caulosaponin.

The specific rotatory power of *caulophyllosaponin* was determined, with the following result:

0.1600, made up to 20 c.c. with absolute alcohol, gave α_D +0°31' in a 2-dm. tube, whence [α]_D +32.3°.

Deca-acetylcaulophyllosaponin, C₆₆H₅₄O₁₇(CO·CH₃)₁₀.—This derivative of *caulophyllosaponin* was prepared by heating it for some time with acetic anhydride, removing the greater part of the latter by distillation, and then pouring the residue into water. An amorphous, white solid was thus deposited, which was extremely soluble in organic solvents, and could not be crystallised. It was first dried in a vacuum desiccator over sulphuric acid and solid potassium hydroxide, and then at 110°, when it melted at 155–160°:

0.1503 gave 0.3565 CO₂ and 0.1074 H₂O. C=64.7; H=7.9.

C₈₆H₁₂₄O₂₇ requires C=65.0; H=7.8 per cent.

*Hydrolysis of Caulophyllosaponin.**Formation of Caulophyllosapogenin, $C_{56}H_{88}O_8(OH)_6$, and Arabinose.*

The hydrolysis of caulophyllosaponin was affected by heating the latter with a 5 per cent. solution of hydrogen chloride in aqueous alcohol for several hours. The alcohol was then removed in a current of steam, and the hydrolytic product, which had separated from the hot liquid in a crystalline state, was collected, the aqueous liquid being put aside for the subsequent examination of the sugar. The crystalline hydrolytic product was recrystallised from dilute pyridine, when it separated in rhombohedral prisms, which decomposed at about 315° :

0.0981 gave 0.2670 CO_2 and 0.0862 H_2O . $C=74.2$; $H=9.8$.

0.1013 „ 0.2748 CO_2 „ 0.0900 H_2O . $C=74.0$; $H=9.9$.

$C_{56}H_{88}O_8$ requires $C=74.3$; $H=9.7$ per cent.

The molecular formula of the above hydrolytic product was established by means of the derivatives described below. It has thus been definitely shown to possess the formula $C_{56}H_{88}O_8$, and to contain six hydroxyl groups, two of which are phenolic. As it is a new compound, it is proposed to designate it *caulophyllosapogenin*.

Caulophyllosapogenin, $C_{56}H_{88}O_8(OH)_6$, possesses physical properties which are very similar to those of the previously described hydrolytic product, *caulosapogenin*. Both these substances decompose at about 315° , and are sparingly soluble in alcohol, but dissolve readily in the latter when containing a little alkali hydroxide. When dissolved in acetic anhydride with a little chloroform, they give a rose-red coloration on the addition of a few drops of concentrated sulphuric acid. *Caulophyllosapogenin*, unlike *caulosapogenin*, does not yield a crystalline benzoyl derivative.

Heza-acetylcaulophyllosapogenin, $C_{56}H_{82}O_9(CO \cdot CH_3)_6$. — This compound was prepared by heating *caulophyllosapogenin* for three hours with an excess of acetic anhydride, then removing the greater portion of the latter, and heating the residue with water in a current of steam. An amorphous solid was thus obtained, which melted at $160-162^\circ$. The substance was extremely soluble in the usual organic solvents, and could not be crystallised, but presumably was homogeneous. An analysis and a determination of its molecular weight gave the following results:

0.0978 gave 0.2517 CO_2 and 0.0795 H_2O . $C=70.2$; $H=9.0$.

0.9613, in 23.63 benzene, gave $\Delta t = 0.180^\circ$. M.W. = 1130.

$C_{56}H_{100}O_{16}$ requires $C=70.6$; $H=8.7$ per cent. M.W. = 1156.

Caulophyllosapogenin Dimethyl Ether, $C_{56}H_{86}O_7(O\cdot CH_3)_2$.—In order to prepare this derivative, caulophyllosapogenin was dissolved in alcohol containing a little potassium hydroxide, and the solution heated with an excess of methyl iodide for several hours. The greater portion of the solvent was then removed, the mixture poured into dilute hydrochloric acid, and the resulting precipitate collected. When crystallised from dilute alcohol, it separated in stellate clusters of small needles, which melted at $240\text{--}242^\circ$:

0.0888 gave 0.2436 CO_2 and 0.0809 H_2O . $C=74.8$; $H=10.1$.

The number of methoxyl groups in the compound was determined by Perkin's modification of Zeisel's method:

0.1547 gave 0.0746 AgI . $MeO=6.4$.

$C_{56}H_{86}O_7(O\cdot CH_3)_2$ requires $C=74.7$; $H=9.9$; $MeO=6.7$ per cent.

Caulophyllosapogenin dimethyl ether is readily soluble in alcohol, ether, chloroform, or benzene. Its specific rotatory power was determined with the following result:

0.1222, made up to 20 c.c. with chloroform, gave $\alpha_D +0.32'$ in a 2-dcm. tube, whence $[\alpha]_D +43.6^\circ$.

*Identification of l-Arabinose, a Hydrolytic Product of
Caulophyllosapogenin.*

The aqueous liquid obtained in the hydrolysis of caulophyllosapogenin, as above described, was exactly neutralised with sodium carbonate, and evaporated to dryness under diminished pressure. The residue was then digested with hot alcohol, the mixture filtered, and to the hot filtrate an equal volume of ethyl acetate was added, when a syrup was deposited. This was removed, and a further quantity of ethyl acetate added to the hot liquid. On keeping the latter for some time, a crystalline substance separated in small, hard nodules, which melted at 156° , and readily reduced Fehling's solution (Found, $C=39.9$; $H=6.9$. $C_5H_{10}O_5$ requires $C=40.0$; $H=6.7$ per cent.).

The optical rotatory power of the substance was determined with the following result:

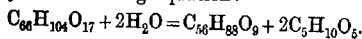
0.1702, made up to 25 c.c. with water, gave $\alpha_D +1.02'$ in a 2-dcm. tube, whence $[\alpha]_D +106.5^\circ$.

The substance yielded an osazone, which, when crystallised from dilute alcohol, was obtained in brownish-yellow needles, melting at 160° (Found, $C=62.2$; $H=6.2$. $C_{17}H_{20}O_3N_4$ requires $C=62.2$; $H=6.1$ per cent.).

From the above results it was evident that the sugar formed by the hydrolysis of caulophyllosapogenin is a pentose, agreeing in all its properties with *l*-arabinose. In order further to confirm its

identity, it was compared with a commercial specimen of arabinose. The latter melted at 156° , and when mixed with the above-described substance no depression in melting point was observed.

The glucoside caulophyllosaponin, $C_{66}H_{104}O_{17}$, is thus seen to be converted by hydrolysis into caulophyllosapogenin, $C_{36}H_{58}O_9$, and *l*-arabinose, $C_5H_{10}O_5$. A known quantity of the glucoside, when hydrolysed by dilute hydrochloric acid in the presence of alcohol, and the alcohol subsequently removed, yielded 72.6 per cent. of its weight of caulophyllosapogenin ($C_{66}H_{104}O_{17}$ requires $C_{36}H_{58}O_9 = 77.4$ per cent.). The hydrolysis of the glucoside is therefore to be represented by the following equation:



*Chloroform, Ethyl Acetate, and Alcohol Extracts of the
Amorphous Material (B).*

Chloroform Extract.—This was a brittle, black solid, amounting to 10.5 grams. It was glucosidic in character, but no definite compound could be isolated from it.

Ethyl Acetate Extract.—This was a greyish-white solid, amounting to 24 grams. It was dissolved in hot alcohol, and the solution kept for some time, when a substance separated in needles, which decomposed at 250 – 255° . This substance was collected, and found to be identical with the previously described glucoside, caulosaponin, $C_{54}H_{88}O_{17}$ (Found, $C=64.0$; $H=8.6$. Calc., $C=64.3$; $H=8.7$ per cent.).

The alcoholic liquid remaining after the separation of the above glucoside was heated with dilute hydrochloric acid, when it yielded a small quantity of caulosapogenin, $C_{42}H_{66}O_6$, decomposing at 315° .

Alcoholic Extract.—This was a brittle, black solid, amounting to 12 grams. It was glucosidic in character, and yielded on hydrolysis a small quantity of caulosapogenin, $C_{42}H_{66}O_6$, which was identified by means of its benzoyl derivative, melting at 288° .

Summary and Physiological Tests.

The material employed for this investigation consisted of the rhizome and roots of *Caulophyllum thalictroides* (Linné), Michaux.

A preliminary test showed the presence of an alkaloid, and a relatively small amount of an enzyme was obtained, which slowly hydrolysed amygdalin.

An alcoholic extract of the ground material, when distilled in a current of steam, yielded a small amount of a pale yellow essential oil. From the alcoholic extract, the following definite compounds were isolated: (i) A crystalline alkaloid, $C_{13}H_{16}ON_2$ (m. p. 137° ;

$[\alpha]_D -221.6^\circ$), which has been identified as methylcytisine; the *picrate* melts at 228° . (ii) A crystalline glucoside, *caulosaponin*, $C_{54}H_{88}O_{17} \cdot 4H_2O$ (m. p. $250-255^\circ$), which yields a *deca-acetyl* derivative, $C_{54}H_{76}O_{17}(CO \cdot CH_3)_{10}$, melting at $135-140^\circ$, and on hydrolysis is resolved into *caulosapogenin*, $C_{42}H_{66}O_8$ (m. p. 315°), and dextrose. Caulosapogenin yields a *tetra-acetyl* derivative, $C_{42}H_{62}O_8(CO \cdot CH_3)_4$, melting at 120° , and a *diacetyl* derivative, $C_{42}H_{64}O_6(CO \cdot CH_3)_2$, melting at $160-162^\circ$, from which a crystalline *monosodio*-derivative, $C_{42}H_{63}O_6Na(CO \cdot CH_3)_2$, was prepared; it yielded, furthermore, a *tetrazobenzoyl* derivative, $C_{42}H_{62}O_6(CO \cdot C_6H_5)_4$, melting at 288° , and a *monomethyl ether*, $C_{42}H_{65}O_5(O \cdot CH_3)$, which melts at 235° . (iii) A new crystalline glucoside, *caulophyllosaponin*, $C_{66}H_{104}O_{17}$ (m. p. $250-260^\circ$; $[\alpha]_D +32.3^\circ$), which yields a *deca-acetyl* derivative, $C_{66}H_{94}O_{17}(CO \cdot CH_3)_{10}$, melting at $155-160^\circ$, and on hydrolysis is resolved into *caulophyllosapogenin*, $C_{56}H_{88}O_9$ (m. p. 315°), and arabinose. Caulophyllosapogenin yields a *hexa-acetyl* derivative, $C_{56}H_{80}O_9(CO \cdot CH_3)_6$, melting at $160-162^\circ$, and a *dimethyl ether*, $C_{56}H_{86}O_7(O \cdot CH_3)_2$, which melts at $240-242^\circ$, and has $[\alpha]_D +43.6^\circ$. (iv) A phytosterol, $C_{27}H_{46}O$ (m. p. 153°). (v) Citrullol, $C_{28}H_{45}O_2(OH)_3$. (vi) A mixture of fatty acids, consisting of palmitic, stearic, cerotic, oleic and linolic acids. The alcoholic extract also contained a quantity of sugar, which yielded *d*-phenylglucosazone (m. p. 210°), and a comparatively small amount of resinous material.

The above-mentioned methylcytisine, $C_{12}H_{15}ON_2$, represents the alkaloid previously obtained by J. U. Lloyd (*Proc. Amer. Pharm. Assoc.*, 1893, **41**, 115), and designated "caulophylline," but he did not succeed in crystallising the base, and its composition was not determined. In view of its present identification, the name "caulophylline" should no longer be retained for this alkaloid.

The compound designated by the present authors as *caulosaponin*, $C_{54}H_{88}O_{17} \cdot 4H_2O$, is undoubtedly identical with a crystalline glucoside first obtained by J. U. Lloyd ("Drugs and Medicines of North America," Vol. II, 1887, p. 151), and termed by him "leontin," although the formula deduced from its analysis was not correct. As it has now been completely characterised, it appears desirable that it should receive the new and distinctive name assigned to it.

For the purpose of determining the physiological action of methylcytisine and the two above-mentioned crystalline glucosides, *caulosaponin* and *caulophyllosaponin*, some tests were kindly conducted for us by Dr. P. P. Laidlaw, of the Wellcome Physiological Research Laboratories, to whom our best thanks may here be expressed.

Methylcytisine has been found to be very similar in its action to

cytisine, but not nearly so potent, the latter being at least ten times as active as the former on the blood pressure of the cat (compare Dale and Laidlaw, *J. Pharmacol. and Exp. Therap.*, 1912, **3**, 205). In other directions, such as the action on the ganglion cells supplying the eye and heart, methylcytisine is also very much weaker than cytisine. On the frog the difference in potency is not so obvious.

The glucosides, caulosaponin and caulophyllosaponin, showed the behaviour of the class of substances known as saponins. Solutions of these substances in physiological salt solution, although very dilute, were found to be powerfully hæmolytic for washed red blood corpuscles, and were also toxic for isolated, perfused frog's hearts. Whole blood and unwashed red blood corpuscles were unaffected, and both glucosides were without action on the frog's heart *in situ*. This difference in action on tissues in the body and on tissues freed from serum is known to be due to lipoid substances in the serum and tissues, for which substances saponins as a class have a marked affinity. The administration of the two glucosides by the mouth to small cats, in doses of 0.1 gram each, resulted in no symptoms of physiological activity other than a mild purgative action after several hours.

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XXIV.—*Quercetagetin*.

By ARTHUR GEORGE PERKIN.

QUERCETAGETIN was isolated from the flowers of the African marigold, *Tagetes patula*, by Latour and Magnier De La Source (*Bull. Soc. chim.*, 1877, [ii], **28**, 337), who state that it also occurs in other varieties of the same plant. In appearance and general properties it is described as resembling quercetin, the colouring matter of quercitron bark, and from this fact, together with its origin, the name *quercetagetin* is evidently derived. On the other hand, according to these authors, its crystalline form, solubility in 60 per cent. alcohol, and the numbers obtained on analysis ($C=58.50$; $H=3.97$) indicated that it was distinct from quercetin, $C_{26}H_{20}O_{12}$, and it was considered to possess the formula $C_{27}H_{22}O_{13}$ (anhydrous), or $C_{27}H_{22}O_{13} \cdot 4H_2O$ (air-dried). In order to isolate the colouring matter from the flowers, boiling 85 per cent. alcohol

was employed, and the deposit, which separated by partly evaporating the liquid, was freed from plant wax and other impurities by extraction with chloroform or carbon disulphide. The crude substance, dissolved in alcohol, was precipitated by water and crystallised from dilute alcohol. Some years ago my attention was directed to the subject by the late Prof. J. J. Hummel, who found that the flowers possessed well-defined tinctorial properties, and a preliminary examination was then carried out (see P., 1902, 18, 75). As attempts to obtain an adequate supply of the flowers were not successful, the work was abandoned for a time, and it is only recently, owing to the kindness of Mr. T. H. Burkill, Reporter on Economic Products to the Government of India, and to Mr. D. Hooper, the Officiating Reporter, to whom I am indebted for several pounds of the petals, that a more complete investigation has been possible. The method adopted for the preparation of the quercetagetin has differed considerably from that employed by its discoverers, it having been recognised that the main quantity of the substance was not present in the free condition in the material, but as glucoside. On the other hand, for purposes of economy, no attempt was made to isolate the glucoside in the pure condition, this being reserved for subsequent investigation.

EXPERIMENTAL.

The petals (1000 grams) were extracted for four hours with ten times their weight of alcohol, the extract evaporated to a small bulk, and poured into water, which caused the separation of viscous matter, possessing an aromatic odour. This was removed by shaking with ether (A), the brownish-yellow aqueous liquid diluted with water to 3500 c.c., and heated to boiling with the addition of 125 c.c. of 33 per cent. hydrochloric acid. On keeping, a small amount of yellow, crystalline substance usually separated, but as the main bulk of the desired compound remained dissolved, this could only be isolated by the tiresome operation of repeated extraction with much ether. After evaporation of the ether, a semi-crystalline, yellow residue remained, and this, by treatment with boiling water and keeping overnight, gave 17.2 grams of very crude colouring matter. It appeared evident from the method of isolation employed by Latour and Magnier De La Source that their product pre-existed in the flowers, for their operations did not involve the hydrolysis of a glucoside, and it was thus to be anticipated that some quantity of the substance was present in the ethereal extract (A). This proved to be the case, for by shaking the ether with dilute sodium carbonate solution, a yellow

liquid was produced, which, when neutralised, gave a precipitate of 4.75 grams of the impure material. To expedite matters, at a later period some quantity of an alcoholic extract of the petals was very kindly prepared by Messrs. Hirst, Brooke, and Hirst, of Leeds, and in operating with this product it was stirred with boiling water, and the viscid, insoluble matter removed by decantation or by filtering through calico. The hydrolysis with hydrochloric acid was carried out at a much greater concentration than that given above, in the expectation that the colouring matter would now be deposited in bulk on cooling, so that the ether treatment could be avoided, but this hope was not realised.

For purification the crude colouring matter from 1000 grams of the petals (22 grams approx.) was treated with 130 c.c. of hot alcohol, filtered from a trace of a sparingly soluble substance (*B*), the filtrate diluted with 90 c.c. of boiling water, and the crystals which had separated overnight were collected and washed with dilute alcohol. The yield was 13.2 grams, or 1.3 per cent., from the petals, and could not be materially increased by working up the filtrate, as this mainly contained a resinous impurity. By recrystallisation from dilute alcohol, the product was now sufficiently pure for most purposes, but for complete purification it was necessary to prepare the acetyl derivative, and after recrystallisation to hydrolyse this with hydrochloric acid in the usual manner. Traces of a substance which formed a more soluble acetyl compound were thus removed, but a loss of some 25 per cent. of material hereby occurred. For analysis, the colouring matter was dried at 160°:

Found, C=56.64, 56.47; H=3.46, 3.31.

* $C_{16}H_{10}O_8$ requires C=56.60; H=3.14 per cent.

As deposited from dilute acetic acid or dilute alcohol, it contains water of crystallisation:

Found, $H_2O=10.10$.

$C_{15}H_{10}O_8 \cdot 2H_2O$ requires $H_2O=10.16$ per cent.

Quercetagetin forms pale yellow, glistening needles or leaflets, closely resembling quercetin in appearance, readily soluble in hot alcohol, and very sparingly so in boiling water. It melts at about 318°, but owing to the darkening of the tube it was difficult to be certain to one degree. Very dilute alkali dissolves it with a pure yellow colour, which by air-oxidation becomes olive, and finally deep brown, but these changes are not so marked when a stronger alkali (10 per cent.) is employed. Alcoholic ferric chloride

* The analyses given by Latour and Magnier De La Source (*loc. cit.*) indicate that their substance contained either a second colouring matter or some other impurity of higher carbon content.

produces an olive-green coloration, whereas cold alcoholic lead acetate forms an orange-red precipitate, which, on keeping, becomes yellower, and finally develops a green tint. The yellow potassium salt precipitated by alcoholic potassium hydroxide rapidly changes to green, and ultimately assumes a brownish-black colour. Quercetagenin does not contain a methoxy-group, and beyond conversion into the hydriodide is unaltered by prolonged digestion with hydriodic acid.

Acetylquercetagenin is readily prepared by digesting quercetagenin with five times its weight of boiling acetic anhydride to which a few drops of pyridine have been added, for one hour. The solution diluted with its own volume of alcohol, on keeping, deposits crystals, which are purified by recrystallisation from a mixture of alcohol and acetic acid. For analysis, the substance (1 gram approx.) in 15 c.c. of acetic acid was hydrolysed by gradual addition of hydrochloric acid (15 c.c.) at the boiling point. Hot water was then added, and the crystals of quercetagenin, which separated on cooling, were collected, and dried at 160° (Found, $C_{15}H_{10}O_8 = 55.61$, 55.82 . $C_{15}H_4O_8(C_2H_3O)_6$ requires $C_{15}H_{10}O_8 = 55.79$ per cent.).

Acetylquercetagenin consists of colourless needles, very sparingly soluble in alcohol. It melts at $209-211^{\circ}$, or slightly higher than was stated previously ($203-205^{\circ}$, *loc. cit.*).

Quercetagenin Sulphate.—Quercetagenin closely resembles in general properties the colouring matters of the flavone group, and readily yields crystalline oxonium compounds when treated with mineral acids in the presence of acetic acid. Of these, only the sulphate, which is deposited in fine orange-coloured needles, was submitted to analysis (Found, $C = 43.28$, 42.69 ; $H = 3.29$, 3.26 . $C_{15}H_{10}O_8 \cdot H_2SO_4$ requires $C = 43.26$; $H = 2.88$ per cent.). By treatment with water, it is converted into quercetagenin and sulphuric acid.

Monopotassium quercetagenin, $C_{15}H_9O_8K$ (Found, $K = 10.74$), separates as an orange-yellow, semi-crystalline precipitate when potassium acetate is added to a solution of quercetagenin in hot absolute alcohol. It possesses the general characteristics of the monosubstituted flavonol salts, and is readily decomposed by boiling water with separation of quercetagenin.

Action of Fused Alkalis on Quercetagenin.—Five grams of quercetagenin were heated with 50 grams of potassium hydroxide and a little water to $200-220^{\circ}$ for half an hour. The product was dissolved in water, the solution neutralised with acid, repeatedly extracted with ether, the extract evaporated, and the dark-coloured viscous residue, which partly solidified on keeping, treated with a little water. When no further separation occurred, the crystals

were collected, drained on a tile, and purified by recrystallisation from water. The colourless needles melted at 194–196°, and possessed the properties of protocatechuic acid.

From the mother liquors no definite phenolic compound could be isolated, and a second alkali fusion at a slightly lower temperature was also fruitless in this respect. As a result of the later experiments described below, there can, however, be no doubt that such a compound is in reality produced during some stage of the hydrolysis, but is subsequently decomposed, probably by oxidation. Although it appeared likely that at a much lower temperature, with weaker alkali and exclusion of air, the desired result might be obtained, it has not been possible to spare sufficient of the rare material for this experiment.

Quercetagetin Pentamethyl Ether, $C_{20}H_{20}O_8$.—Quercetagetin (8 grams) dissolved in methyl alcohol (100 c.c.) was treated with excess of methyl iodide (50 c.c.), the mixture boiled, and a solution of potassium hydroxide (16 grams) in methyl alcohol added, drop by drop, during fourteen hours, this procedure being adopted as in the case of myricetin (T., 1902, 81, 245) with the object of preventing an oxidation which readily occurs in the presence of the alkali. After removal of the unattacked methyl iodide and the greater portion of the alcohol by distillation, the residue was treated with ether, and the solution washed with water. By now shaking with dilute alkali, a dull yellow extract was obtained, which, on acidification, yielded a semi-crystalline precipitate. The residual ethereal liquid (*B*) was reserved for subsequent examination. The product was collected and purified by crystallisation from alcohol:

Found, C=61·93, 61·85; H=5·58, 5·34; CH_3 =19·40.
 $C_{17}H_{16}O_8(O\cdot CH_3)_5$ requires C=61·86; H=5·15; CH_3 =19·33 per cent.

It consisted of pale yellow needles, melting at 161–162°, sparingly soluble in cold alcohol, and insoluble in cold alkaline solutions. If, however, to the pentamethyl ether suspended in dilute potassium hydroxide solution a little alcohol is added, the crystals now readily dissolve on shaking with the production of a yellow liquid, and the isolation of this compound in the manner above described was evidently due to the occurrence of some alcohol in the ether. Boiling concentrated potassium hydroxide solution also dissolves this compound, and on cooling, the potassium salt separates as a yellow, colloidal precipitate. With sulphuric acid, quercetagetin pentamethyl ether forms a yellow liquid, which is reddened by the addition of nitric acid.

Acetylquercetagetin pentamethyl ether crystallises from acetic

anhydride in colourless needles, melting at $161-163^{\circ}$, and its solution in alcohol possesses a faint blue fluorescence.

Quercetagetin Hexamethyl Ether, $C_{21}H_{25}O_8$.—The ethereal liquid (B), containing that portion of the methylation product undissolved by dilute alkali, was evaporated, and the viscous residue treated with a little methyl alcohol. On keeping overnight, the crystals, which had then separated, were collected and recrystallised from the same solvent. The pale yellow product melted indefinitely between 130° and 140° , and as experiment indicated it to be a mixture of the pentamethyl ether with a second substance, to remove the former it was repeatedly crystallised from dilute alcoholic potassium hydroxide. In this manner, colourless, prismatic needles eventually separated, which melted at $141-143^{\circ}$, and appeared to be pure, but by recrystallisation from acetone the melting point rose to $157-158^{\circ}$:

Found, C=62.74; H=5.50; $CH_3=22.22$.

$C_{17}H_{21}O_8(O\cdot CH_3)_6$ requires C=62.68; H=5.47; $CH_3=22.38$ per cent.

The compound forms colourless needles, sparingly soluble in cold alcohol. The yield was extremely poor, although a considerable excess of alkali and iodide had been employed for the methylation, an indication that by this method it can only be produced with difficulty.

As it was desirable to prepare, if possible, some quantity of this hexamethyl ether, experiments were carried out on the action of methyl sulphate on the dry potassium salt of the pentamethyl compound, such a method having given good results in the case of quercetin (Waliaschko, *Arch. Pharm.*, 1904, **242**, 242) and myricetin (*loc. cit.*). 0.8 Gram of quercetagetin pentamethyl ether was added to a solution of 0.5 gram of potassium hydroxide in a little alcohol, the mixture evaporated to dryness, ground with 1.25 grams of methyl sulphate, and, after remaining overnight, treated with a further quantity of the sulphate. At the end of the second day, the product was washed with ether, digested with boiling water, and crystallised from dilute alcoholic potassium hydroxide. The colourless, prismatic needles melted at $141-142^{\circ}$, but after recrystallisation from acetone at $157-158^{\circ}$, and consisted of quercetagetin hexamethyl ether, which, it thus seems probable, may be dimorphous. The yield (0.2 gram) was, however, again poor, and this could only be accounted for by the fact that the salt of pentamethyl ether, being soluble in alcohol, suffers hydrolysis during the evaporation of the solution to dryness. On the other hand, the salts of the corresponding quercetin and myricetin compounds are insoluble and not so readily attacked in this manner.

Quercetagetin Hexaethyl Ether, $C_{27}H_{31}O_8$.—It has been shown,

in the case of myricetin (*loc. cit.*), and more recently with quercetin and other flavone colouring matters (P., 1912, 28, 328), that by the employment of excess of ethyl iodide and alkali, no difficulty is experienced in obtaining from these compounds good yields of their fully ethylated derivatives. A similar method was accordingly applied to quercetagetin, in the hope that a better result would be given than was the case with the methylation process. Ten grams of quercetagetin in 140 c.c. of alcohol were treated with 60 c.c. of ethyl iodide, and to the boiling mixture a concentrated solution of 24 grams of potassium hydroxide in alcohol was added, drop by drop, during two days. After removal of the unchanged ethyl iodide and the greater portion of the alcohol, the residual liquid was poured into ether, the solution washed with water, then with dilute alkali, and evaporated. The almost colourless, crystalline product, which melted at 135–137°, was dissolved in hot alcohol, a few drops of alcoholic potassium hydroxide were added, and the crystals, which separated on cooling, were collected. The pale yellow tint of the filtrate indicated the presence of a trace of the potassium salt of the pentaethyl compound. When obtained in this way, the substance was usually pure, and melted at 139–141°, but a second treatment was sometimes necessary. The yield was 6.35 grams:

Found, C=66.44; H=7.43; Et=35.47.

$C_{18}H_{24}O_2(OEt)_6$ requires C=66.66; H=7.00; Et=35.80 per cent.

Quercetagetin hexaethyl ether forms colourless needles, sparingly soluble in cold alcohol. With mineral acids in the presence of boiling acetic acid, it readily yields oxonium compounds, the sulphate separating in orange needles, whereas the crystals of the hydrochloride possessed a somewhat more yellow colour. This behaviour is analogous to that of quercetin pentamethyl ether (Watson, P., 1911, 27, 163).

Hydrolysis of Quercetagetin Hexaethyl Ether.—If quercetagetin were in reality a flavonol derivative, the gentle hydrolysis of its hexaethyl derivative, by means of alcoholic potassium hydroxide, should, as has been previously shown to be the case with quercetin (Herzig, Ber., 1909, 42, 155) and myricetin (*loc. cit.*), yield products affording proof of such a structure.

Five grams of the substance, dissolved in a hot solution of 10 grams of potassium hydroxide in 50 c.c. of 80 per cent. alcohol, were heated on the steam-bath for seven hours. The liquid, which did not solidify on keeping (distinction from quercetin and myricetin), was evaporated to dryness, the residue dissolved in water, and the solution saturated with carbon dioxide. An oily product (A) thus separated, which was removed by ether, and

weighed approximately 2.7 grams. The aqueous liquid, on acidification, gave a colourless, crystalline precipitate (*B*) (2.23 grams), and this was purified by recrystallisation (Found, $C=62.55$; $H=7.04$; $Et=26.70$. $C_6H_3(OEt)_2 \cdot CO_2H$ requires $C=62.85$; $H=6.66$; $Et=27.61$ per cent.). It melted at $167-169^\circ$, and consisted of protocatechuic acid diethyl ether. The oily product (*A*), which only yielded crystals after keeping for some weeks, was drained on tile, and crystallised two or three times from minute amounts of methyl alcohol, the only solvent found suitable for the purpose, but in which it is somewhat readily soluble:

Found, $C=61.22$; $H=7.75$; $Et=36.71$.

$C_{16}H_{22}O_6$ requires $C=61.53$; $H=7.69$; $Et=37.17$ per cent.

This substance, for which the name of *quercetagetol tetraethyl ether* is suggested, consists of prismatic needles, melting at $46-48^\circ$, soluble, although not very readily, in dilute alkali, indicating the presence of a free hydroxyl group. With acetic anhydride in the usual manner, it gave an oily acetyl compound, which up to the present has not become crystalline.

As it was to be anticipated that this compound contained a carbonyl group and should thus yield an oxime, a mixture of 0.56 gram of the substance, 1 gram of anhydrous sodium acetate, and 0.25 gram of hydroxylamine hydrochloride was digested with 25 c.c. of boiling alcohol for four hours (compare Lapworth and Steele, T., 1911, 99, 1884). After removal of the alcohol, the residue, on treatment with water, gave to ether an oily product, which on long keeping solidified, and was repeatedly crystallised from a mixture of light petroleum and carbon disulphide:

Found, $C=58.74$; H_2O lost; $N=4.38$.

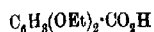
$C_{16}H_{25}O_6N$ requires $C=58.71$; $N=4.28$ per cent.

This *oxime* consists of colourless needles, melting at $93-95^\circ$.

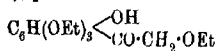
With the object of obtaining further indication of the constitution of the quercetagetol tetraethyl ether, 1 gram, dissolved in 50 c.c. of 2 per cent. potassium hydroxide solution, was gradually treated with a cold solution of 3 grams of potassium permanganate in 50 c.c. of water. Oxidation readily took place, but towards the end of the operation the pink coloration very slowly disappeared. The mixture was filtered, the precipitated oxide exhausted with boiling water, the clear liquid when cold saturated with carbon dioxide, and extracted with ether to remove traces of unattacked substance (if present). From the aqueous solution after acidification, ether now removed a small amount of a crystalline acid, and this, when recrystallised from water, formed colourless, prismatic needles, melting at $100-102^\circ$, with the production of a

clear liquid, which commenced to effervesce between 129° and 136°. Sufficient of this compound was unfortunately not available for analysis, but for purposes of future study, it will be referred to as *quercetagetinic acid*.

Quercetagetin hexaethyl ether thus yields by the above-described method of hydrolysis diethylprotocatechuic acid (I), and a ketone, quercetagetol tetraethyl ether, which there is little reason to doubt, in view of the previous study of quercetin pentaethyl ether and myricetin hexaethyl ether (*loc. cit.*), possesses the constitution (II):

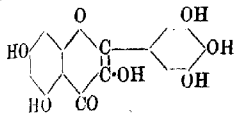


(I.)

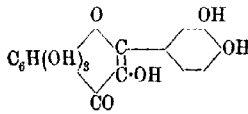


(II.)

Quercetagetin is indeed, as its general reactions also indicate, a hexahydroxyflavonol isomeric with myricetin. It differs, however, from this colouring matter, and also from the closely allied quercetin in possessing a tetrahydroxybenzene nucleus in place of the phloroglucinol nucleus which they contain, as the following formulae indicate:



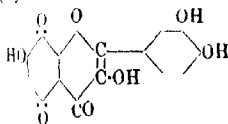
Myricetin.



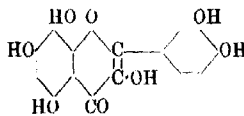
Quercetagetin.

With regard to the exact position of the hydroxyl groups in the tetrahydroxybenzene nucleus of quercetagetin, which could occupy the positions: $\text{O}:\text{OH}:\text{OH}:\text{OH} = 1:2:3:4, 1:3:4:5, 1:2:3:5,$ or $1:2:4:5$, the evidence is scanty, and may be especially difficult to ascertain in the case of so rare a colouring matter.

According to Nierenstein and Wheldale (*Ber.*, 1911, **44**, 3487), quercetin when oxidised by chromic acid gives the quinone, quercetone (I), which by reduction is converted into the flavonol (II):



(I.)



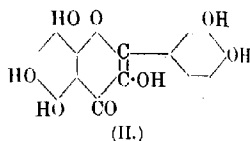
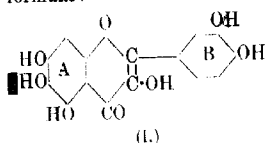
(II.)

but as the latter compound melts at 352—359°, its methyl ether at 147—149°, sintering at 136—138°, and the acetyl compound could not be crystallised, it cannot therefore be quercetagetin.

On the other hand, the fact that quercetagetin pentamethyl ether is insoluble in alkali suggests that in this compound the unmethylated hydroxyl group occupies the position (5) and is adjacent to the carbonyl group, although this again cannot yet be regarded

as certain because, whereas quercetagetin yields, although with difficulty, a hexamethyl derivative, no fully methylated flavonol compound possessing an hydroxyl group in this position has previously been obtained by the employment of methyl iodide and alkali. It is to be noted, however, that in almost every instance of this group hitherto studied a phloroglucinol nucleus has been present in the substances which it is quite reasonable to suppose might exert an influence in this respect not possessed by a tetrahydroxybenzene group.

From a consideration of these points, it thus appears likely that quercetagetin is to be represented by one or other of the following formulæ:



Of these the second seems, at first sight, most probable, because should quercetagetin possess the pyrogallol grouping present in I, a more rapid oxidation of the substance in alkaline solution, with accompanying colour change, as in the case of myricetin, would be expected.

Dyeing Properties.—As is to be anticipated from its constitution quercetagetin readily dyes mordanted fabrics shades of a generally similar character to those given by other well-known flavonol colouring matters. A comparison of the dyeings given by this compound and quercetin on mordanted woollen cloth are, however, interesting, in that colours yielded by the former possess a distinctly yellower character.

	Chromium.	Aluminium.	Tin.	Iron.
Quercetagetin	Dull olive-yellow	Yellow-orange	Brown	Brownish-black
Quercetin.....	Orange-yellow	Bright orange	Reddish-brown	Olive-black

This result is somewhat remarkable in that it has been previously shown that fisetin (trihydroxy-), quercetin (tetrahydroxy-), and myricetin (pentahydroxy-flavonol) yield practically identical colours, unless the duller and yellower shades given by quercetagetin are ascribed to slight oxidation during the dyeing process. This, however, does not appear to be the case, for when chalk is employed during the operation no marked change of shade is observed, as is the case when dyeing with gossypetin (T., 1899, 75, 828). An important point in this respect is that quercetagetin, whatever tetrahydroxybenzene group it may contain, possesses attached respectively to the nuclei A and B pairs of ortho-hydroxyl groups, each

of which is capable of inducing a strong tinctorial effect with mordants. With a compound of this constitution, containing as it does only a single chromophore, according to the quinonoid theory only one of these pairs can influence the dyeing operation, although it is to be conceived that the quinonoid arrangement might vary in distinct lake particles. Thus, whereas it appears certain and has been discussed in former communications that in quercetin the shades are mainly the result of the effect of the ortho-hydroxyl groups in its catechol nucleus (*B*), it is probable, on the other hand, that the yellow colours given by quercetagenin are governed by the hydroxyl groups present in the nucleus (*A*).

The more sparingly soluble colouring matter from the flowers, which was present in the crude quercetagenin to the extent of about 1 per cent., resembled rhamnetin (quercetin monomethyl ether) in appearance, but was not, as seemed probable, a methyl ether of quercetagenin, for hydriodic acid indicated the absence of a methoxy-group. When crystallised from alcohol, it forms somewhat indefinite groups of minute needles, and dissolves in alkaline solutions with an orange colour, passing to green on dilution with water. Owing to the minute amount available, no further examination of this compound was attempted.

Dyeing Properties of the Flowers.—Employing mordanted woollen cloth, the following shades were obtained:

Chromium.	Aluminium,	Tin.	Iron.
Yellowish-brown	Pale dull yellow	Deep yellow-orange	Brownish-black

These possessed a somewhat redder character than those given by quercitron bark, and were similar to, although not so red as, those from patent bark. In this case the tinctorial effect is mainly due to glucoside.

Further work with quercetagenin will be carried out as soon as opportunity occurs, and an investigation of the isomeric and closely allied colouring matter gossypetin is in progress, the results of which it is anticipated will throw further light on the exact structure of both compounds.

CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS.

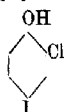
XXV.—*The Chlorination of Iodophenols. Part II.*
The Chlorination of o-Haloid Derivatives of
p-Iodophenol.

By GEORGE KING, M.Sc. (Priestley Research Scholar of the University of Birmingham), and HAMILTON McCOMBIE.

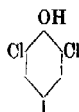
It has been shown by Brazier and McCombie (T., 1912, 101, 968) that *p*-iodophenol (I), when treated with chlorine in a cold carbon tetrachloride solution, yielded an unstable dichloride, which decomposed rapidly, evolving hydrogen chloride and forming 2-chloro-4-iodophenol (II):



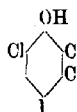
(I.)



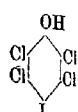
(II.)



(III.)



(IV.)



(V.)

This iodophenol, in turn, when chlorinated, gave an unstable dichloride, which, on decomposition, yielded 2:6-dichloro-4-iodophenol (III). This phenol was converted, by successive stages, into 2:3:6-trichloro- (IV) and 2:3:5:6-tetrachloro-4-iodophenol (V).

In contradistinction to the phenols, the acyl derivatives yielded relatively stable iodo-dichlorides. The iodo-dichlorides of all the benzoyl derivatives were found to remain perfectly stable for months, whilst those of the acetyl derivatives could be kept for several days before any decomposition took place.

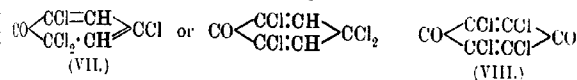
The work has now been extended to a study of various derivatives of *p*-iodophenol, in which one or both of the ortho-positions relative to the hydroxyl group are occupied by halogen atoms.

The first compound studied was 2:4:6-tri-iodophenol (VI). Willgerodt (Ber., 1892, 25, 3495) states that 2:4:6-tri-iodophenol, when chlorinated in chloroform solution, gave an oily substance, and seems to have been under the impression that, both in this case and in the case of *o*-iodophenol, chlorination results in the displacement of iodine in the molecule by chlorine. The authors have found, however, that, when pure tri-iodophenol is chlorinated in a dilute carbon tetrachloride solution, a dichloride could be isolated. This dichloride, although unstable, was much more stable than those derived from *p*-iodophenol and its chloro-substitution products, and differed further from these compounds in that, on decomposition, chlorine was eliminated and tri-iodophenol was regenerated.

The relative stability of the dichlorides of the acyl derivatives of

p-iodophenol finds its parallel also in the case of tri-iodophenol. The acetyl derivatives of tri-iodophenol yielded, on chlorination, a dichloride, which decomposed only after being kept in a sealed tube for six weeks exposed to sunlight. The dichloride of the benzoyl derivative has remained stable for a period of twelve months.

Since, in the present research, the dichloride of tri-iodophenol has been obtained when employing solutions in carbon tetrachloride, whilst Willgerodt, by using chloroform as solvent, obtained a product in which iodine was substituted by chlorine, it seemed probable, when considering the stability of the dichloride, that the effect of the solvent had to be taken into consideration, and accordingly a study of the influence of the solvent on the chlorination has been made. It has been found that, by the use of a suitable solvent, a dichloride of tri-iodophenol could be obtained, whilst, by employing other media for chlorination, displacement of iodine by chlorine took place. Among the solvents employed, it was found that chlorination in carbon tetrachloride and in light petroleum yielded the dichloride, whilst in ether, in chloroform, and in glacial acetic acid, gave rise to products in which the iodine was replaced by chlorine. In the latter group of solvents, the influence of glacial acetic acid was fully investigated, and it was found that four distinct substances were obtained, namely: (1) a red, oily substance, constituting about 1 per cent.; (2) tetra-chlorocyclohexadienone (VII), constituting about 90 per cent.; (3) chloroanil (VIII), about 6 per cent.; (4) a colourless substance, melting at 110°, and containing 66 per cent. of chlorine.



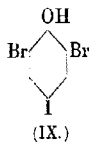
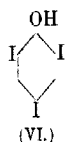
Brazier and McCombie (*loc. cit.*, p. 977) identified traces of chloroanil as one of the products which result when chlorine acts on *p*-iodophenol in carbon tetrachloride at 50–60°. It has also been noticed by the authors that small quantities of chloroanil are produced when 2:4-di-iodophenol is chlorinated. In the case of tri-iodophenol, a copious yield of chloroanil was obtained when chlorination took place in boiling acetic acid solution, and it is interesting to note that a similar displacement of bromine by chlorine has been observed in glacial acetic acid solution (Benedikt and Schmidt, *Monatsh.*, 1883, 4, 604).

Hence, in considering the action of chlorine on tri-iodophenol, it is to be noted that both the solvent and the temperature have a marked influence on the products.

The interesting fact that, although the dichloride of *p*-iodophenol

decomposed with evolution of hydrogen chloride and the formation of chloriodophenol, the dichloride of tri-iodophenol gave off chlorine with regeneration of tri-iodophenol, led the authors to examine the behaviour of other *p*-iodophenols, in which the positions 2 and 6 are occupied by halogen atoms. Brazier and McCombie have shown that both 2-chloro-4-iodophenol (II) and 2:6-dichloro-4-iodophenol (III) yield unstable iodo-dichlorides, which decompose with evolution of hydrogen chloride.

In the first place, the authors examined the behaviour towards chlorine of 2:6-dibromo-4-iodophenol (IX), which was easily prepared by means of the diazo-reaction from the corresponding amino-compound. This compound yields an iodo-dichloride, the stability of which was very similar to that of the tri-iodo-compound, also, on decomposition, chlorine was evolved, and the original dibromo-iodophenol was regenerated. Thus it is seen that, with two iodine or with two bromine atoms in the 2:6-position of *p*-iodophenol, the iodo-dichlorides decompose with evolution of chlorine, whilst, if there are two chlorine atoms in these positions, hydrogen chloride is evolved, and ring substitution takes place. In some way or another, the two bromine and two iodine atoms are able to protect the hydrogen atoms in position 3 and 5 from attack by the chlorine resulting from the decomposition of the iodo-dichloride.

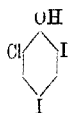


The next compound which was examined was 2:4-di-iodophenol (X). This substance, on treatment with chlorine, yielded an iodo-dichloride which was more unstable than the corresponding compound derived from tri-iodophenol, but was very similar, in its behaviour, to the dichloride derived from *p*-iodophenol. Like that compound, it decomposed with evolution of hydrogen chloride, and the formation of a chloriodophenol. The product was 6-chloro-2:4-di-iodophenol (XI); the proof of this constitution was furnished by the conversion of the decomposition product, by means of nitric acid, into 6-chloro-2:4-dinitrophenol. This compound has been described by various investigators, and its constitution is undoubted (compare Griess, *Annalen*, 1859, 109, 286; Faust and Müller, *ibid.*, 1874, 173, 312; Faust and Saame, *Annalen Suppl.*, 1869-70, 7, 195; Seifart, *ibid.*, 197; Brazier and McCombie, *loc cit.*).

Di-iodophenyl acetate yields an iodo-dichloride, which is less stable than the corresponding tri-iodo-derivative, for, whilst the

latter remained stable for six weeks, the former, under similar conditions, decomposed in ten days. When the dichloride of di-iodophenyl acetate did decompose, hydrogen chloride was given off, whilst in the case of the tri-iodo-compound, chlorine was evolved. The benzoyl derivative of di-iodophenol yielded a very stable iodo-dichloride, behaving in that respect similarly to the benzoyl derivatives of all the *p*-iodophenols which have been studied.

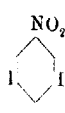
In this study of the chlorination of di-iodophenol, and of tri-iodophenol, and their simple acyl derivatives, it has always been found, by analysis, that only one of the iodine atoms becomes multi-valent. Since it has been shown by Willgerodt and Desaga (*Ber.*, 1904, **37**, 1301) that *m*-di-iodobenzene unites with chlorine in two



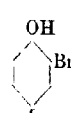
(XI.)



(XII.)



(XIII.)



(XIV.)

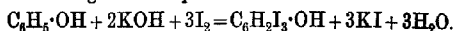
stages to form the compounds $C_6H_4I \cdot ICl_2$ and $C_6H_4(ICI_2)_2$, it seems as if the hydroxyl group in these polyiodo-phenols exerted a protective influence over one or more of the iodine atoms. The influence thus exerted by the hydroxyl and the acyl groups is similar to that of the methyl group, observed by Willgerodt and Simonis (*Ber.*, 1906, **39**, 269), who state that 3:4-di-iodotoluene (XII) yields only a mono-iodo-dichloride. Another instance of the destruction of the tervalency of an iodine atom is furnished by the behaviour of 3:5-di-iodonitrobenzene (XIII). Willgerodt and Ernst (*Ber.*, 1901, **34**, 3406) were able to prepare only a mono-iodo-dichloride from this compound, the negative nitro-group having destroyed the tervalency of one of the iodine atoms in the same way as the positive methyl group did in 3:4-di-iodotoluene.

The last derivative of *p*-iodophenol which was studied was 2-bromo-4-iodophenol (XIV). This compound, on chlorination, was found to behave in the same way as did 2:4-di-iodophenol, 2-chloro-4-iodophenol, and 2:6-dichloro-4-iodophenol. Hydrogen chloride was evolved, and 6-chloro-2-bromo-4-iodophenol was produced.

In considering the stability of the iodo-dichlorides described in this paper, it is to be noticed that various factors exert different influences. In the preparation of the iodo-dichlorides, it is found that, if the chlorine is not very dry, either the iodo-dichloride is not formed, or, if it is formed, it is unstable. Again, if the iodo-dichlorides are placed in sealed tubes, they are found to decompose

much more rapidly than if they are left exposed to the air. The effect of light on the decomposition was studied, but this was found to have practically no influence. The stability is also influenced very largely by the purity of the iodo-dichloride, the effect of impurities on the stability being markedly less when substitution of chlorine in the nucleus takes place. Provided very pure products were chlorinated, and the iodo-dichloride after being separated was washed thoroughly with carbon tetrachloride and dried rapidly on a porous plate, it was found possible to determine the melting points of these compounds with a fair degree of accuracy. In this manner the following melting points, not elsewhere recorded, have been determined: *p*-iodophenol dichloride, 63—64°; 2-chloro-4-iodophenol dichloride, 62—64°; 2:6-dichloro-4-iodophenol dichloride, 58—60°.

The preparation of 2:4:6-triiodophenol has been described by Körner (*Annalen*, 1866, **137**, 213), Messinger and Vortmann (*Ber.*, 1889, **22**, 2313), Brenans (*Compt. rend.*, 1901, **132**, 831), and Carrasco (*Boll. chim. farm.*, 1908, **47**, 109). After an extended investigation of the various methods, it was found most satisfactory to work according to the equation:



The production of tri-iodophenol depends on the amount of potassium hydroxide present, and the yield is good when a large excess of potassium hydroxide is employed, since the potassium salt is formed directly. This method, however, is not an economical one, since all the potassium iodide is lost. In the presence of a moderate excess of potassium hydroxide, the main product is not tri-iodophenol, but the red tetraiodo-diphenylenequinone (compare Lautemann, *Annalen*, 1861, **120**, 309; Wilkie, *J. Soc. Chem. Ind.*, 1911, **30**, 398; 1912, **31**, 208).

EXPERIMENTAL.

The method used for the continuous preparation of 2:4:6-tri-iodophenol was as follows. To 600 c.c. of an 8 per cent. potassium iodide solution containing 38.1 grams of iodine, 3.1 grams of phenol dissolved in 20 c.c. of water were added, 5.6 grams of potassium hydroxide in 150 c.c. of water were poured slowly down the sides of the flask, and the solution was shaken thoroughly. After remaining for not more than three hours, the precipitate was collected, and the filtrate, containing excess of iodine and potassium iodide, was reserved for a second preparation. (For subsequent preparations, 25 grams of iodine were dissolved in the filtrate, and the same quantities of phenol and potassium hydroxide as above

were added.) The precipitate was dissolved in potassium hydroxide, and the tri-iodophenol reprecipitated with 30 per cent. hydrochloric acid, when it was obtained in a granular condition, and free from the red quinone which often accompanies it. By fractional precipitation from methylated spirit by the addition of water up to a dilution of 40 per cent., 10 to 12 grams of tri-iodophenol, melting at 155–156°, were obtained.

Action of Chlorine on 2:4:6-Tri-iodophenol: Influence of the Solvent and the Temperature.

This chlorination was carried out in different solvents, and under different conditions of temperature.

In Carbon Tetrachloride Solution.—Chlorine was bubbled slowly through an ice-cold 0.7 per cent. solution of the tri-iodophenol in carbon tetrachloride, and the yellow precipitate which appeared was separated. The precipitate was found to possess all the properties of an iodo-dichloride, and melted and decomposed at 55–60°. After a short time, the compound decomposed slowly, chlorine and some hydrogen chloride being evolved. The mass resulting from the decomposition contained free iodine, but when recrystallised from a mixture of methyl alcohol and water, gave pure tri-iodophenol.

In order to study the influence of temperature on this chlorination, chlorine was led into a 20 per cent. solution of tri-iodophenol in carbon tetrachloride at 50°. Much iodine was liberated, and when the passage of chlorine was continued, a dark red powder was precipitated. This product was rich in iodine and chlorine, and completely volatile; it was most probably iodine monochloride.

The solution, on concentration, yielded a yellow oil, which was soluble in dilute potassium hydroxide, and, although not an iodo-dichloride, contained a large amount of chlorine, which had probably displaced some or all of the iodine atoms.

In Chloroform and Ether.—Even from an ice-cold 20 per cent. solution of tri-iodophenol in these solvents, no iodo-dichloride could be isolated; only an oily substance was obtained (compare above, and Willgerodt, *Ber.*, 1892, **25**, 3494).

In Light Petroleum.—The iodo-dichloride was obtained when light petroleum was used as solvent.

In Glacial Acetic Acid.—A slow stream of chlorine was bubbled through a solution of tri-iodophenol in glacial acetic acid at 15°. After from six to eight minutes,* when the solution had darkened

* It was noticed repeatedly that if water were added after one minute, a red substance was precipitated; this was stable in air, and contained no free iodine. Methyl alcohol changed the mass to pale yellow, the alcohol remaining colourless.

considerably with liberated iodine, cold water was added, when a light yellow mass was precipitated. This precipitate consisted of: (1) A red, oily substance, forming about 1 per cent. of the precipitate; (2) tetrachlorocyclohexadienone (VII), constituting about 90 per cent. of the precipitate; (3) chloroanil, about 6 per cent.; (4) a colourless substance, which melted at 110° , and contained 66 per cent. of chlorine.

The separation of these four substances was effected by means of methyl alcohol, which retained the oily compound in solution, whilst the chloroanil and the colourless substance crystallised out from the solution. By the addition of water to the filtrate, the tetrachlorocyclohexadienone was precipitated, and when crystallised from a mixture of methyl alcohol and water, separated in very long, pale yellow needles, melting at $121-122^{\circ}$. This was identical with the compound obtained by Zincke (*Ber.*, 1894, **27**, 545) (Found, Cl=61.02. Calc., Cl=61.7 per cent.).

Although chlorination of tri-iodophenol in cold acetic acid gave a small yield of chloroanil, a theoretical yield of this substance was obtained by passing a rapid stream of chlorine for three hours through a boiling concentrated solution. It was sparingly soluble in the acetic acid, and, on cooling, crystallised in large, flat plates, which, when recrystallised from benzene, separated in long, yellow needles, melting at 285° (Found, Cl=57.2. Calc., Cl=57.7 per cent.).

In attempting to determine the nature of this compound, a small quantity was treated with phenylhydrazine in absolute alcohol. Much nitrogen was evolved, and the substance obtained, when crystallised from a mixture of methyl alcohol and water, separated in pale brown needles, melting at $229-230^{\circ}$, and containing 55.4 per cent. of chlorine. A similar reaction has been noticed by Purgotti (*Gazzetta*, 1894, **24**, 554) when chloroanil is treated with hydrazine hydrate, but both these reactions require further investigation.

2:4:6-Tri-iodophenyl Acetate, $C_6H_2I_3 \cdot OAc$.

Tri-iodophenol was acetylated by the action of acetic anhydride in the presence of a drop of sulphuric acid (compare Orton and Smith, T., 1908, **93**, 1247). When crystallised from benzene, chloroform, or glacial acetic acid, it separated in long needles, melting at 153° .

The *dichloride* was prepared in carbon tetrachloride solution, and formed as a yellow incrustation, which melted and decomposed at $144-147^{\circ}$. For analysis, a specimen was prepared from the

pure acetyl derivative, and was washed thoroughly with carbon tetrachloride:

0.1743 gave 0.2981 $\text{AgCl} + \text{AgI}$.

$\text{C}_8\text{H}_5\text{O}_2\text{I}_3$ requires $\text{AgCl} + \text{AgI} = 0.2956$.

A small quantity of this iodo-dichloride was sealed up and exposed to sunlight. After six weeks it slowly decomposed with the liberation of a little iodine. The product, when crystallised from a mixture of methyl alcohol and water, consisted of tri-iodophenyl acetate.

2:4:6-Tri-iodophenyl Benzoate, $\text{C}_6\text{H}_2\text{I}_3\cdot\text{OBz}$.

Since some difficulty was experienced in preparing this compound by the Schotten-Baumann reaction (compare Brazier and McCombie, *loc. cit.*, p. 970), benzylation in pyridine was employed. The product, when crystallised from acetone, separated in large, transparent plates, melting at 137° (Found, $\text{I} = 66.01$. Calc., $\text{I} = 66.15$ per cent.).

The dichloride was obtained from carbon tetrachloride solution as a yellow incrustation, which melted and decomposed at $132-134^\circ$.

0.0946 gave 0.1419 $\text{AgCl} + \text{AgI}$.

$\text{C}_{12}\text{H}_7\text{O}_2\text{Cl}_2\text{I}_3$ requires $\text{AgCl} + \text{AgBr} = 0.1451$.

This iodo-dichloride has remained stable for a period of twelve months. On treating the compound with 10 per cent. potassium hydroxide, no iodoso-compound was formed, but the benzoyl derivative was regenerated.

2:6-Dibromo-4-iodophenol, $\text{C}_6\text{H}_3\text{Br}_2\text{I}\cdot\text{OH}$ (IX).

2:6-Dibromo-4-aminophenol, obtained by the bromination of *p*-nitrophenol and subsequent reduction with tin and hydrochloric acid (Möhlau, *Annalen*, 1895, **289**, 95), was converted into the corresponding iodophenol by means of the diazo-reaction. 2:6-Dibromo-4-iodophenol is moderately volatile in steam, and can be separated by this means from the mixture after diazotisation and the addition of potassium iodide. When crystallised from light petroleum, or from a mixture of methyl alcohol and water, it separates in long, transparent needles, melting at 105° :

0.0972 gave 0.1546 $\text{AgBr} + \text{AgI}$.

$\text{C}_6\text{H}_3\text{OBr}_2\text{I}$ requires $\text{AgBr} + \text{AgI} = 0.1571$.

The dichloride was prepared in a 20 per cent. carbon tetrachloride solution, and separated, when chlorine had been passed through the solution for three hours, in bright yellow needles, melting at 63° :

0.0666 gave 0.1306 $\text{AgCl} + \text{AgBr} + \text{AgI}$.

$\text{C}_6\text{H}_3\text{OCl}_2\text{Br}_2\text{I}$ requires $\text{AgCl} + \text{AgBr} + \text{AgI} = 0.1332$.

The whole of the chlorine in this iodo-dichloride was shown to be attached to the multivalent iodine atom by estimating the iodine liberated when the iodo-dichloride in methyl-alcoholic solution reacted with potassium iodide. Titration with sodium thiosulphate gave $\text{Cl}=14.92$.

$\text{C}_6\text{H}_3\text{OCl}_2\text{Br}_2\text{I}$ requires $\text{Cl}=15.5$ per cent.

The dibromo-iodophenol, precipitated during the titration, was identified and weighed.

This iodo-dichloride was found to remain stable during three days, but then gradually decomposed with liberation of chlorine. Examination of the decomposition product showed it to be dibromo-iodophenol.

2: 6-Dibromo-4-iodophenyl Acetate, $\text{C}_6\text{H}_2\text{Br}_2\text{I}\cdot\text{OAc}$.

This compound was obtained by acetylation in presence of a drop of sulphuric acid. When crystallised from a mixture of methyl alcohol and water, it separated in long, colourless needles, melting at 87° :

0.0974 gave 0.1410 $\text{AgBr} + \text{AgI}$.

$\text{C}_8\text{H}_5\text{O}_2\text{Br}_2\text{I}$ requires $\text{AgBr} + \text{AgI}=0.1419$.

The *dichloride* was exceptionally difficult to obtain, and was precipitated only after passing chlorine for two days through a concentrated carbon tetrachloride solution. It consisted of stable, bright yellow, feathery needles, which melted and decomposed at $116-117^\circ$:

0.0312 gave 0.0567 $\text{AgCl} + \text{AgBr} + \text{AgI}$.

$\text{C}_8\text{H}_5\text{O}_2\text{Cl}_2\text{Br}_2\text{I}$ requires $\text{AgCl} + \text{AgBr} + \text{AgI}=0.0571$.

2: 6-Dibromo-4-iodophenyl Benzoate, $\text{C}_6\text{H}_2\text{Br}_2\text{I}\cdot\text{OBz}$.

This compound was prepared by the pyridine method, and when crystallised from the mixture of methyl alcohol and water, separated in short, colourless, prismatic needles, melting at 97° :

0.0486 gave 0.0623 $\text{AgBr} + \text{AgI}$.

$\text{C}_{13}\text{H}_7\text{O}_2\text{Br}_2\text{I}$ requires $\text{AgBr} + \text{AgI}=0.0616$.

The *dichloride*, obtained by chlorinating for half an hour, was stable, granular, yellow powder, melting and decomposing at $123-125^\circ$:

0.0501 gave 0.0806 $\text{AgCl} + \text{AgBr} + \text{AgI}$.

$\text{C}_{13}\text{H}_7\text{O}_2\text{Cl}_2\text{Br}_2\text{I}$ requires $\text{AgCl} + \text{AgBr} + \text{AgI}=0.0814$.

Dichloride of 2:4-Di-iodophenyl Acetate, $\text{Cl}_2\text{I}\cdot\text{C}_6\text{H}_3\cdot\text{OAc}$.

This substance was obtained as a pale yellow, granular precipitate when chlorine was led into a 20 per cent. solution of 2:4-di-iodophenyl acetate in carbon tetrachloride. It melted and decomposed at $127-130^\circ$:

0.1124 gave 0.1871 $\text{AgCl} + \text{AgI}$.

$\text{C}_8\text{H}_5\text{O}_2\text{Cl}_2\text{I}_2$ requires $\text{AgCl} + \text{AgI} = 0.1858$.

After remaining in a sealed tube for ten days without undergoing any visible change, this iodo-dichloride decomposed, spontaneously generating a considerable pressure of hydrogen chloride.

2:4-Di-iodophenyl Benzoate, $\text{C}_6\text{H}_3\text{I}_2\cdot\text{OBz}$.

This derivative was prepared by the action of 1 gram of benzoyl chloride on 1.5 grams of di-iodophenol dissolved in 4 c.c. of pyridine. On pouring the solution into dilute sulphuric acid, the benzoate was precipitated, and when crystallised from methyl alcohol or from light petroleum, separated in needles, melting at 98° (Found, $\text{I} = 56.3$. Calc., $\text{I} = 56.44$ per cent.).

The *dichloride* was obtained as a very pale yellow, granular powder, melting and decomposing at $134-135^\circ$:

0.1034 gave 0.1501 $\text{AgCl} + \text{AgI}$.

$\text{C}_{13}\text{H}_5\text{O}_2\text{Cl}_2\text{I}_2$ requires $\text{AgCl} + \text{AgI} = 0.1503$.

This iodo-dichloride, like that of tri-iodophenyl benzoate, was exceptionally stable, and has remained so for over six months. Attempts to prepare the iodoso-compound regenerated the benzoyl derivative.

Action of Chlorine on 2:4-Di-iodophenol: Preparation of 6-Chloro-2:4-di-iodophenol, $\text{C}_6\text{H}_3\text{OClI}_2$.

The di-iodophenol required for these experiments was prepared from *p*-iodophenol according to the method described by Neumann (*Annalen*, 1887, **241**, 79).

A slow stream of chlorine was passed through an ice-cold solution of 10 grams of di-iodophenol in 300 c.c. of carbon tetrachloride, resulting in the precipitation of 11 grams of an orange-yellow iodo-dichloride, which melted and decomposed at $59-61^\circ$. Precipitation was complete in five to ten minutes, and the separated solid was quickly transferred to a flat dish cooled in ice. Energetic decomposition took place immediately, hydrogen chloride being evolved and some iodine liberated. When the iodine had volatilised, there remained a light brown, semi-solid mass, weighing 2.5 grams. Since recrystallisation yielded only oily products, the decomposition

product obtained from several chlorinations was treated with sodium hydrogen sulphite and distilled in a current of steam. If steam was passed slowly through the mixture, a solid product was obtained. This substance, after several recrystallisations from light petroleum, separated in colourless needles, melting at 99° . The yield was 22 per cent. of the theoretical:

0.1262 gave 0.2014 $\text{AgCl} + \text{AgI}$.

$\text{C}_6\text{H}_3\text{OClI}_2$ requires $\text{AgCl} + \text{AgI} = 0.2030$.

The mixed haloids were oxidised with potassium dichromate and sulphuric acid, chlorine was liberated, and the silver iodate formed was reduced with sulphurous acid (compare McNair, T., 1893, 63, 1052), but this method was found to give results for iodine 1 to 2 per cent. too low:

Found, $\text{I} = 65.24$.

$\text{C}_6\text{H}_3\text{OClI}_2$ requires $\text{I} = 66.74$ per cent.

The constitution of this chlorodi-iodophenol was determined by heating the compound with concentrated nitric acid in the presence of a few drops of sulphuric acid. Much iodine was liberated, and on pouring into sodium hydrogen sulphite solution and extracting with ether, 6-chloro-2:4-dinitrophenol, melting at 112° , was obtained.

On chlorinating 6-chloro-2:4-di-iodophenol, an iodo-dichloride was obtained in slender, pale yellow plates, melting and decomposing at 50° . After some time, the compound decomposed with liberation of hydrogen chloride. Owing, however, to the poor yields which were obtained, this decomposition was not followed any further.

6-Chloro-2:4-di-iodophenyl Acetate, $\text{C}_6\text{H}_2\text{ClI}_2\cdot\text{OAc}$.

When prepared by means of acetic anhydride and sulphuric acid, this compound was obtained in theoretical yield, and, after three crystallisations from a mixture of methyl alcohol and water, separated in colourless needles, melting at $74-75^{\circ}$:

0.0872 gave 0.1274 $\text{AgCl} + \text{AgI}$.

$\text{C}_6\text{H}_3\text{O}_2\text{ClI}$ requires $\text{AgCl} + \text{AgI} = 0.1267$.

Estimation of the iodine by oxidation of the mixed haloids gave $\text{I} = 58.7$. Calc., $\text{I} = 60.1$ per cent.

The dichloride consisted of pale yellow, feathery needles, melting and decomposing at 110° :

0.0807 gave 0.1467 $\text{AgCl} + \text{AgI}$.

$\text{C}_6\text{H}_3\text{O}_2\text{Cl}_2\text{I}$ requires $\text{AgCl} + \text{AgI} = 0.1472$.

After being kept in a sealed tube for three and a-half days, this

iodo-dichloride decomposed rapidly, with evolution of hydrogen chloride. Attempts to prepare the iodoso-compound failed, chloro-iodophenyl acetate being regenerated.

6-Chloro-2:4-diiodophenyl Benzoate, $C_6H_3ClI_2 \cdot OBz$.

This compound was prepared by both the pyridine and the Schotten-Baumann method. In both cases a product was obtained, which, after long keeping, solidified partly, and melted at about 32° , but could not be crystallised.

The *dichloride* was a yellow, granular powder, which melted and decomposed at $117-119^\circ$:

0.0432 gave 0.0680 $AgCl + AgI$.

$C_{13}H_7O_2Cl_2I_2$ requires $AgCl + AgI = 0.0700$.

Attempts to regenerate the benzoate from the iodo-dichloride gave only oily products.

2-Bromo-4-iodophenol, $C_6H_3BrI \cdot OH$.

o-Bromophenol was nitrated, and the mixture of nitro-compounds (4-nitro- and 6-nitro-) was separated by steam distillation. 2-Bromo-4-nitrophenol, on reduction, gave the amino-compound which by means of the diazo-reaction yielded 2-bromo-4-iodophenol, which was obtained from the mixture by distillation in a current of steam.

2-Bromo-4-iodophenol is very soluble in all ordinary organic solvents, but is only sparingly so in water, crystallising from it in long, colourless needles; crystallisation from light petroleum gave short, white, prismatic needles, melting at 51° :

0.1081 gave 0.1504 $AgBr + AgI$.

C_6H_4OBrI requires $AgBr + AgI = 0.1529$.

2-Bromo-4-iodophenyl Acetate, $C_6H_3BrI \cdot OAc$.

This compound is very soluble in methyl and ethyl alcohols, but crystallises from light petroleum in clusters of ill-defined, rectangular plates, melting at 52° :

0.0909 gave 0.1142 $AgBr + AgI$.

$C_8H_5O_2BrI$ requires $AgBr + AgI = 0.1127$.

The *dichloride* was obtained only after continuous chlorination for six hours. It forms a golden-yellow incrustation, which melts and decomposes at 113° :

0.0353 gave 0.0623 $AgCl + AgBr + AgI$.

$C_8H_5O_2Cl_2BrI$ requires $AgCl + AgBr + AgI = 0.0608$.

Action of Chlorine on 2-Bromo-4-iodophenol: Preparation of 6-Chloro-2-bromo-4-iodophenol, $C_6H_2ClBrI \cdot OH$.

2-Bromo-4-iodophenol was chlorinated in 20 per cent. carbon tetrachloride solution for forty minutes, when the iodo-dichloride was precipitated in bright yellow needles, melting and decomposing at $69-70^\circ$. After washing with carbon tetrachloride, the iodo-dichloride was found to remain stable for about forty-five minutes. Rapid decomposition then took place, sufficient heat being evolved to melt the decomposition product. The free iodine liberated during the decomposition was removed, and the product was purified by solution in alcohol and precipitation with water. The substance is very soluble in alcohol and most other organic solvents, but crystallised slowly from light petroleum. By seeding with the product thus obtained, crystallisation was effected from a mixture of methyl alcohol and water, when the substance separated in colourless needles, melting at $81-82^\circ$:

0.0322 gave 0.0542 $AgCl + AgBr + AgI$.

$C_6H_2OClBrI$ requires $AgCl + AgBr + AgI = 0.0547$.

On further chlorination of 6-chloro-2-bromo-4-iodophenol, the *dichloride* separated in bright yellow, feathery needles, melting and decomposing at $66-67^\circ$. After remaining at room temperature for two hours, this iodo-dichloride darkened and became oily; hydrogen chloride was evolved in the decomposition.

Attempts were made to prepare the acetyl derivative of 6-chloro-2-bromo-4-iodophenol, but it could not be crystallised satisfactorily. The iodo-chloride separated as a pale yellow, granular precipitate, melting and decomposing at $102-103^\circ$.

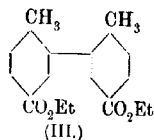
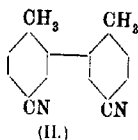
CHEMICAL DEPARTMENT,
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BIRMINGHAM.

XXVI.—2 : 2'-Ditolyl-5 : 5'-dicarboxylic Acid.

By JAMES KENNER and ERNEST WITHAM.

IN connexion with investigations on 2 : 2'-ditolyl (Kenner and Turner, T., 1911, **99**, 2101; Kenner, P., 1912, **28**, 187), it was decided to attempt the preparation of nuclear-substituted derivatives of this substance. The present paper contains an account of the synthesis of 2 : 2'-ditolyl-5 : 5'-dicarboxylic acid, and certain of its derivatives, from those of *o*-iodo-*p*-toluic acid by treatment with copper powder according to Ullmann's well-known process.

The iodotoluic acid just mentioned has already been described by Kloeppel (*Ber.*, 1893, **26**, 1733), who obtained it from the corresponding amino-derivative, but as it was desired to examine the behaviour of its nitrile towards copper powder, the latter substance (I) was first prepared from *o*-amino-*p*-toluonitrile, described by Banse (*Ber.*, 1894, **27**, 2163) and Borsche (*Ber.*, 1903, **36**, 4359). This compound, and the methyl and ethyl esters of the carboxylic acid obtained by its hydrolysis, were then heated with copper powder, and respectively converted into 5:5'-dicyano-2:2'-ditolyl (II), diethyl 2:2'-ditolyl-5:5'-dicarboxylate (III), and the corresponding dimethyl ester:

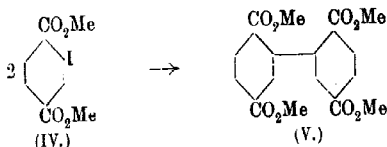


It may be remarked that the preparation of the 5:5'-dicyano-derivative is the first instance in which Ullmann's method has been applied to an iodonitrile, and it was found that the success of the operation in this case, and, indeed, in the other two cases now described, required careful attention to the conditions of the experiment. In each case the iodo-derivative must be heated to the requisite temperature as rapidly as possible, and the duration of the treatment with copper powder should not be extended beyond a certain length of time, which varies with the substance. Prolonged heating leads to the formation of tarry products, from which the desired compound cannot be isolated. It has also been the invariable experience of one of us that tarry products of high boiling point result in the preparation of 2:2'-ditolyl, for which somewhat prolonged heating is prescribed by Ullmann. The formation of such by-products probably occurs to a greater or less extent in all reactions of this type, and is presumably due to secondary reactions, in which the excess of copper powder used in the condensation plays the part of a catalyst.*

When the experiments now described were well advanced, a paper

* The presence of small amounts of moisture and fat in the "Naturkupper-C" used in our experiments (compare Schlenk, Mair, and Bornhardt, *Ber.*, 1911, **44**, 1172, footnote; and Schmidlin, *Ber.*, 1912, **45**, 3176, footnote) may conceivably be partly responsible for the formation of tarry matter, but the explanation suggested above appears to us to be more probable. For examples of the catalytic action of copper, see, *inter alia*, Knoevenagel and Heckel, *Ber.*, 1903, **36**, 2823; Salatiel and Benderens, *Ann. Chim. Phys.*, 1905, [viii], **4**, 347; *Compt. rend.*, 1901, **132**, 1333; Ullmann, *Ber.*, 1905, **38**, 729, 2120, 2211; Ipatiev, *Ber.*, 1909, **42**, 2089, 2098; 1910, **43**, 3337.

appeared (*Ber.*, 1912, **45**, 1187) in which Liebermann described the results of his investigation of the action of oxalyl chloride on derivatives of diphenyl in the presence of aluminium chloride. In the case of 2:2'-ditolyl, the sole product isolated was a dicarboxylic acid, to which the constitution of a 5:5'-dicarboxylic acid was provisionally assigned. The properties of the acid (m. p. 287°) and of its dimethyl ester (m. p. 124°) do not, however, agree with those of our synthetical products, which respectively melt above 300° and at 134°, and we were therefore disinclined to accept Liebermann's formula. To reassure ourselves on this point, dimethyl iodo-terephthalate (IV) was converted by treatment with copper powder into tetramethyl diphenyl-2:5:2':5'-tetracarboxylate (V), in order that a comparison might be instituted with the tetramethyl ester prepared by Liebermann from the oxidation product of his ditolyl-dicarboxylic acid.



In this case, also, the synthetical product melted considerably higher than Liebermann's compound, and, leaving out of account the possibility of an isomerism of the type recently observed by Cain, Coulthard, and Micklethwait (*T.*, 1912, **101**, 2298), it would appear that the series of compounds isolated by Liebermann must have a different constitution from that originally attributed to them.

The remaining possibilities (assuming a symmetrical structure) are that the carboxyl groups may be in the 3:3', the 4:4', or the 6:6'-positions. The first of these is excluded by the non-identity of the tetramethyl ester (m. p. 141°) of the tetracarboxylic acid, obtained by oxidation, with the synthetical tetramethyl diphenyl-2:3:2':3'-tetracarboxylate (m. p. 161°), recently described by one of us (*P.*, 1912, **28**, 277). The second possibility is rejected by Liebermann, whilst the properties of the synthetical 2:2'-ditolyl-6:6'-dicarboxylic acid, described by Mayer (*Ber.*, 1911, **44**, 2303), together with the absence of any 4:5-dimethylphenanthraquinone from the products of the reaction, show that this formula is also untenable. Liebermann's compound would appear, therefore, to possess an unsymmetrical structure, and this suggestion derives support from the fact that the acid obtained, together with 2:7-dimethylphenanthraquinone, by the action of oxalyl chloride

on 4:4'-ditolyl, is considered by Liebermann also to be unsymmetrical.*

EXPERIMENTAL.

o-Iodo-*p*-toluonitrile, $C_6H_3MeI-CN$.

A solution of 45 grams of *o*-amino-*p*-toluonitrile in 900 c.c. of 10 per cent. sulphuric acid was cooled to 0° , and diazotised with a solution of 23 grams of sodium nitrite in 60 c.c. of water. On the gradual addition of a solution of 80 grams of potassium iodide in 140 c.c. water, the iodo-compound rapidly separated and solidified. It was washed with hot sulphurous acid solution and hot dilute sodium hydroxide solution, and then crystallised from ethyl acetate. The yield was 60 per cent. of the calculated. The compound may also be crystallised from light petroleum (b. p. $90-110^\circ$), but this solvent is less effective in removing small amounts of a red compound (probably azotoluonitrile), which accompanies the main product.

o-Iodo-*p*-toluonitrile forms magnificent colourless, rhombic crystals, melting at 57.5° , and is readily soluble in ether, chloroform, or hot alcohol:

0.3526 gave 0.3433 AgI. $I=52.6$.

C_6H_3NI requires $I=52.26$ per cent.

o-Iodo-*p*-toluic acid, $C_6H_3MeI \cdot CO_2H$, resulted when the above nitrile was boiled for three and a-half hours with 10 parts of 15 per cent. sodium hydroxide solution, and the solution, after cooling and dilution, was acidified. The acid, after crystallisation from alcohol, melted at $205-206^\circ$, and agreed in its properties with those described by Kloeppel (*Ber.*, 1893, **26**, 1734) (Found, $C=36.64$; $H=2.62$. M.W.=263. Calc., $C=36.64$; $H=2.67$ per cent. M.W.=262). Its barium, ferric, cobalt, and lead salts are sparingly, its calcium salt moderately, soluble in hot water, whilst its magnesium salt is readily soluble.

The methyl ester, prepared by esterification with sulphuric acid, boils at $194^\circ/52$ mm., and slowly solidifies to a mass of crystals, melting at 28° :

0.3254 gave 0.4676 CO_2 and 0.0998 H_2O . $C=39.16$; $H=3.41$.

0.2827 „ 0.2423 AgI. $I=45.83$.

$C_6H_3O_2I$ requires $C=39.13$; $H=3.26$; $I=46.01$ per cent.

* In view of this result, tetramethyl diphenyl-3:4:3':4'-tetracarboxylate has recently been prepared in this laboratory by Miss A. M. Mathews, B.Sc., from dimethyl 4-iodophthalate, and as its properties were found to correspond with those of the product obtained by Liebermann in his experiments with 3:3'-ditolyl, the symmetrical structure assigned by him in this case appears to be confirmed.—J. K.

The *ethyl* ester, prepared in a similar manner, boils at $242^{\circ}/175$ mm.:

0.3482 gave 0.5288 CO_2 and 0.1174 H_2O . $\text{C}=41.42$; $\text{H}=3.75$.

0.3460 „ 0.2801 AgI. $\text{I}=43.75$.

$\text{C}_{10}\text{H}_{11}\text{O}_2\text{I}$ requires $\text{C}=41.38$; $\text{H}=3.83$; $\text{I}=43.79$ per cent.

The *amide* crystallises from alcohol in leaflets, melting at 167° :

0.1590 gave 7.8 c.c. N_2 at 20° and 722 mm. $\text{N}=5.45$.

$\text{C}_8\text{H}_8\text{ONI}$ requires $\text{N}=5.37$ per cent.

The *hydrazide* crystallises from alcohol in prisms, melting at 151° . It is readily soluble in chloroform, but sparingly so in ether or light petroleum:

0.1618 gave 14.6 c.c. N_2 at 16° and 733 mm. $\text{N}=10.33$.

$\text{C}_8\text{H}_8\text{ON}_2\text{I}$ requires $\text{N}=10.02$ per cent.

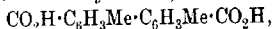
5: 5'-*Diacyano-2: 2'-ditolyl*, $\text{CN}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CN}$, was prepared by rapidly heating *o*-iodo-*p*-toluonitrile to 260° , and adding an equal weight of copper powder in portions at intervals during ten minutes. The temperature was maintained at 260° for fifteen minutes longer, during which time the mixture was kept well stirred, and the product was then cooled and extracted with benzene. After concentration, light petroleum (b. p. $90-110^{\circ}$) was added until no more oily matter was precipitated, and the almost colourless solution was then allowed to crystallise by spontaneous evaporation. The nitrile was further purified by crystallisation from ethyl acetate, and was thus obtained in leaflets, melting at 159° . The yield of pure material was small. The compound was readily soluble in chloroform, ether, or hot alcohol, but only sparingly so in light petroleum:

0.1400 gave 0.4235 CO_2 and 0.0670 H_2O . $\text{C}=82.50$; $\text{H}=5.32$.

0.1570 „ 16.8 c.c. N_2 at 15° and 739 mm. $\text{N}=12.39$.

$\text{C}_{16}\text{H}_{12}\text{N}_2$ requires $\text{C}=82.71$; $\text{H}=5.17$; $\text{N}=12.07$ per cent.

2: 2'-*Ditolyl-5: 5'-dicarboxylic acid*,



readily resulted on hydrolysis of its esters with alcoholic potassium hydroxide. It is only moderately soluble in alcohol, and separates from this solvent in a microcrystalline condition. Its melting point lies above 300° :

0.1230 gave 0.3182 CO_2 and 0.0590 H_2O . $\text{C}=71.3$; $\text{H}=5.3$.

0.1324 required 9.7 c.c. $\text{N}/10\text{-NaOH}$. $\text{M.W.}=273$

$\text{C}_{16}\text{H}_{14}\text{O}_4$ requires $\text{C}=71.11$; $\text{H}=5.2$ per cent. $\text{M.W.}=270$.

Its barium, calcium, cobalt, and mercuric salts, as well as those of the alkali metals, are soluble in water, whilst the ferric and lead salts are only sparingly soluble.

The *dimethyl* ester was prepared by gradual addition, in the space of twenty minutes, of copper powder to an equal weight of methyl *o*-iodo-*p*-toluate at 260°, and heating the mixture further for half an hour. After cooling, the product was extracted with ether, and the crude product thus obtained amounted to 65 per cent. of the calculated quantity. It was further purified by crystallisation from light petroleum (b. p. 60–80°), and finally from methyl alcohol. It forms prisms, melting at 133°:

0.1450 gave 0.3844 CO₂ and 0.0786 H₂O. C = 72.3; H = 6.02.

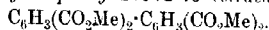
C₁₈H₁₈O₄ requires C = 72.48; H = 6.04 per cent.

The *diethyl* ester, prepared in a similar manner, was separated from the copper powder by extraction with ether, and after crystallisation the crude product was drained on porous earthenware. The yield was 55 per cent. of the calculated. It was further purified by crystallisation from light petroleum (b. p. 40–60°), in which medium it is readily soluble, and was thus obtained in small prisms, melting at 76°:

0.1288 gave 0.3474 CO₂ and 0.0765 H₂O. C = 73.4; H = 6.59.

C₂₀H₂₀O₄ requires C = 73.62; H = 6.75 per cent.

Tetramethyl Diphenyl-2:5:2':5'-tetracarboxylate,



Dimethyl iodoterephthalate was required for the synthesis of this compound, and was prepared by saturating a suspension of 20 grams of iodoterephthalic acid in 200 c.c. of cold methyl alcohol with hydrogen chloride, and finally warming the mixture on the water-bath until complete solution had taken place. The pure ester, melting at 80°, separated on cooling, and a further quantity was obtained from the mother liquor. Abbes (*Ber.*, 1893, 26, 2952) gives the melting point as 77–78°.

The addition of copper powder to this ester at 260° was followed by a vigorous reaction and a rise in temperature to 310°. After an equal weight of copper powder had been gradually added to the ester in the course of twenty minutes, the mixture was heated for a further forty-five minutes. After cooling, the mass was extracted with hot benzene, from which tetramethyl diphenyltetracarboxylate separated in the pure condition. It forms small prisms, melting at 156°. The yield amounted to 70 per cent. of that calculated, and would probably have been greater still if precautions had been taken in view of the tendency to sublimation exhibited by this compound:

0.1410 gave 0.3208 CO₂ and 0.0616 H₂O. C = 62.45; H = 4.85.

C₂₀H₁₈O₄ requires C = 62.18; H = 4.85 per cent.

The ester was easily hydrolysed by alcoholic potassium hydroxide, and the acid was isolated in the usual manner.

Diphenyl-2:5:2':5'-tetracarboxylic acid melts above 300° , and is remarkable for its very sparing solubility in the usual solvents, in contrast with the ready solubility of its isomerides. It reacts, however, with cold sodium hydrogen carbonate solution. For analysis it was dried at 180° :

0.1562 gave 0.3304 CO_2 and 0.0464 H_2O . $\text{C} = 57.69$; $\text{H} = 3.30$.

0.1070 required 12.87 c.c. $\text{N}/10\text{-NaOH}$. $\text{M.W.} = 332.6$.

$\text{C}_{16}\text{H}_{10}\text{O}_8$ requires $\text{C} = 58.18$; $\text{H} = 3.03$ per cent. $\text{M.W.} = 330$.

In conclusion, we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which defrayed the greater part of the cost of this investigation.

THE UNIVERSITY,
SHEFFIELD.

XXVII. — *The Action of Ammonia and Alkylamines on Reducing Sugars.*

By JAMES COLQUHOUN IRVINE, ROBERT FRASER THOMSON,
M.A., B.Sc., and CHARLES SCOTT GARRETT, B.Sc.

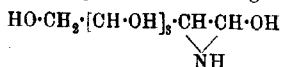
THE abundant literature which has accumulated on the action of alkalis on carbohydrates is an index of the importance attached to such inquiries, and shows that attention has been specially directed to the reaction between ammonia and the reducing sugars. This is particularly the case since the discovery of the amino-sugar, glucosamine, and many researches were apparently based on attempts to produce compounds of this type by simple condensation.

Considering the views at present held regarding the constitution both of reducing sugars and of glucosamine, it is not surprising that in no case has the latter compound been obtained by the direct action of ammonia on a hexose. The products actually formed are frequently complex. In some instances definite additive compounds seem to be produced, but generally condensation proceeds through loss of a molecule of water, and the ultimate production of the so-called "imines" of the sugars.

As the constitution generally assigned to compounds of this type seemed to us to be inconsistent with the results obtained in this laboratory on the condensation of sugars and amino-compounds, we considered it advisable to re-investigate the problem. In particular the constitution of glucoseimine is a question of some

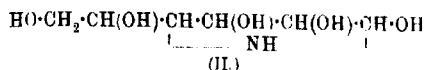
importance in view of the isomerism of the compound with glucosamine, and in throwing light on the structure of the analogous arabinoseimine from which Fischer prepared glucosaminic acid (*Ber.*, 1902, **35**, 3787) as one of the steps in the synthesis of glucosamine.

Lobry de Bruyn, who first isolated glucoseimine (*Ber.*, 1895, **28**, 3082), ascribed to the compound the following structure:



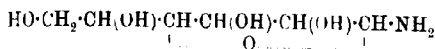
(I.)

This was subsequently modified by Wohl, who holds that an imino-group connects the γ -carbon atoms:



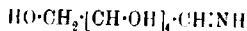
(II.)

On the other hand, the formula for arabinoseimine which best explains the relationship between this compound and glucosaminic acid is one in which an amino-group is directly attached to the terminal carbon atom of the chain, and this leads to a third alternative formula for glucoseimine:



(III.)

The remaining possibility, which represents the compound as an imino-glucose, is derived from the hypothetical aldehyde ammonia compound by loss of a molecule of water:



(IV.)

We have endeavoured to discriminate between these four alternatives, and, although all the results obtained are not entirely consistent, the bulk of the evidence points to formula III as being the most suitable. The two imino-ring formulæ are rejected on the ground that ammonia is without action on alcoholic solutions of sucrose or of α -methylglucoside. Negative evidence of a more conclusive nature was afforded by the fact that tetramethyl- α -methylglucoside is similarly unaffected by the action of alcoholic ammonia. In this case all the hydroxy-positions in the parent sugar are substituted, and only the oxygen atom of the ring is available for condensation. Even in the case of such a highly reactive compound as gluconolactone, we find that the action of ammonia gives rise to gluconamide, and no cyclic nitrogen derivatives were formed. The collective evidence of these results shows that the condensation under discussion is confined to the reducing group of the free sugar

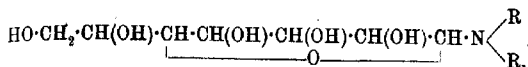
This limits the alternatives to formulæ III and IV, either of which might result from the dehydration of an aldehyde ammonia derivative. No positive evidence, however, exists of the formation of additive compounds of this type from glucose, as Stone's results have been called in question by Lobry de Bruyn.

On account of the ease with which glucoseimine is hydrolysed, it is difficult to obtain satisfactory evidence of the presence of the amino-group. Nitrogen is certainly evolved on the addition of nitrous acid, but this is doubtless preceded by the removal of a molecule of ammonia from the compound. The reducing action, and the absence of the property of salt formation, which is so characteristic of glucosamine, we have now shown to be due to the same cause. Further consideration of all four formulæ indicates that the compound ought either to exhibit mutarotation or to exist in two stereoisomeric forms which are not spontaneously interconvertible. The detection of mutarotation in solution is thus, in this particular instance, of little value in distinguishing between formulæ III and IV, but the fact that we have observed this phenomenon is in accordance with the former alternative, as it brings the compound into line with glucoseanilide and other similar derivatives. Our observations of mutarotation were, however, not very decisive, owing to the instability of the compound and the speed with which equilibrium is attained, or a combination of these factors.

Attempts to prepare glucoseimine synthetically from specific α - and β -derivatives of glucose led to a curious result. The action of ammonia in ethereal solution on α - and β -penta-acetylglucoses gave in each case acetamide, and the imino-biose described by Sjollem (Rec. trav. chim., 1899, 18, 292). Considering the conditions adopted in these experiments, which were carried out in the cold, it is evident that the action of the ammonia is not confined to hydrolysis of the acetyl groups and subsequent reaction with the unsubstituted sugar. The imino-biose is, in fact, only formed when glucoseimine is heated, and, moreover, free glucose could not have been formed in the reaction as it is quite insoluble in ether. The imino-biose must therefore have resulted from the loss of one molecule of ammonia from two molecules of tetra-acetylglucoseimine, and the acetyl groups were only removed in the final stage of the reaction. Similarly, the action of ammonia on tetra-acetyl-*l*-eromoglucose also gave rise to the imino-biose, together with acetamide and ammonium bromide. This result is also significant as an index that the amino-group in glucoseimine occupies the glucosidic position in the sugar residue.

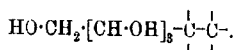
The evidence thus obtained in favour of formula III was supplemented by the study of the behaviour of glucose towards

alkylamines. Only on the analogy of this formula should condensation of the sugar with secondary amines take place. We find that glucose reacts with difficulty with ethylamine, diethylamine, and dimethylamine, giving, in the first-mentioned case, a crystalline ethylaminoglucose which exhibits measurable mutarotation. These condensations thus give products of the following general type:

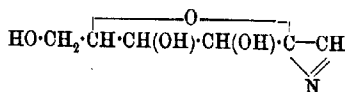


The action of ammonia on an alcoholic solution of fructose was also studied, as the results obtained by Lobry de Bruyn, in which he isolated the compound $\text{C}_{12}\text{H}_{20}\text{O}_8\text{N}_2$, did not seem to admit of any simple explanation. We have confirmed his results, and also added to the complexities involved in this reaction by the isolation of a second product, $\text{C}_6\text{H}_2\text{O}_4\text{N}$. This substance is quite inactive, but is nevertheless not a derivative of glucose, as it is converted into glucosephenylosazone displaying the normal activity. This points to extremely complex reactions resulting when nitrogen is introduced into the penultimate position in the ketose molecule. The change must here, as in many other cases when sugars are acted on by alkaline reagents, be accompanied by oxidation.

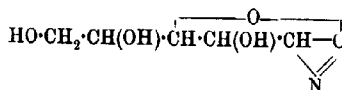
The constitution of the compound $\text{C}_6\text{H}_2\text{O}_4\text{N}$ is indicated by the fact, mentioned above, that it is converted into glucosephenylosazone, as this result suggests the presence of the grouping:



It is, however, evident that the hydrogen and oxygen content demand a rearrangement to the corresponding γ -oxidic structure. Nitrogen must thus connect the two terminal carbon atoms, and two alternatives remain:



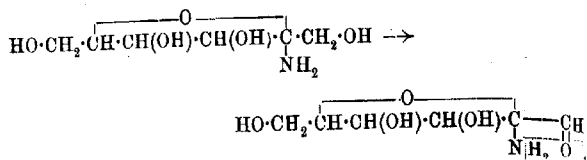
(I.)



(II.)

Between these alternatives we are unable to discriminate, but formula I is to be preferred, as the formation of the compound

probably involves the following decomposition of the unknown fructoseimine:



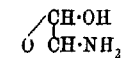
This view was supported by the fact that the same inactive compound was produced by the action of ammonia, in methyl-alcoholic solution, on glucosone. It will also be seen that the relationship between this compound and 2:5-ditetrahydroxybutylpyrazine, which is the main product of the action of ammonia on fructose, is a fairly simple one.

The most notable property of the compound, for which the name fructoseazine is suggested, is its stability towards acids. When heated with 2 per cent. aqueous hydrogen chloride for several hours, it remained quite unaltered, and, for this reason, we have discarded any alternative formula involving coupling of the hexose residues. The above behaviour is in sharp contrast to the ready hydrolysis of glucoseimine or the glucosealkylimines. The nitrogen is, however, easily expelled in the form of ammonia by the action of alkalis.

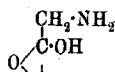
It is evident that the derivatives of sugars containing amino- or substituted amino-groups may be divided into two classes. In the one class, which includes glucosamine and isoglucosamine, the reducing group is unsubstituted, the compounds do not undergo hydrolytic changes when heated with acids, and thus possess the property of salt formation. In glucoseimine and the related compounds, nitrogen occupies the reducing position, and hydrolysis with acids takes place so readily that definite salts cannot be isolated.

This remarkable difference in stability seems to be due to the relative positions occupied by nitrogen with reference to the reducing group. Stable compounds are, in fact, only formed when nitrogen is linked to the carbon atom directly connected to the reducing group. Substitution of the reducing group, or of any hydroxyl group other than that adjacent to it, results in unstable products. The essential difference in structure shown by typical members of each of these two classes is shown below:

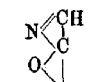
Class A (Stable).



Glucosamine.

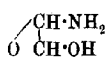


isoGlucosamine.

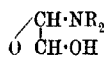


Fructoseazine.

Class B (Unstable).



Glucoseimine.



Alkylaminoglucoses.



Fischer's aminoglucose.*

The simple structural difference between the types A and B seems at first sight insufficient to account for the great difference in properties. It must, however, be remembered, that the reducing group in sugars is distinctly acidic, and may thus combine with an amino-group, which is favourably situated, so as to form a second internal ring in the molecule. These conditions are realised in the case of glucosamine (Class A), for which we have previously, on perfectly independent grounds, suggested a ring structure (T., 1912, 101, 1128), but are excluded in the compounds included under B, which must thus be regarded as open-chain amino- or substituted amino-glucoses.

The conclusions drawn above receive a certain amount of support by the fact that the aminoglucose corresponding with the amino-methylglucoside recently isolated by Fischer (*loc. cit.*) is, compared with the isomeric glucosamine, considerably less stable to acids. In this case, the reducing group of the sugar is unsubstituted, and the amino-group occupies the ϵ -position. Further, as already indicated, the compound $\text{C}_6\text{H}_{10}\text{O}_4\text{N}$, for which a ring structure containing nitrogen is now deduced, is perfectly stable when boiled with dilute acids.

EXPERIMENTAL.

Mutarotation of Glucoseimine.

The glucoseimine was prepared by the method described by Lobry de Bruyn (*loc. cit.*). In each experiment, 50 grams of glucose were dissolved in 700 c.c. of methyl alcohol previously

* So far, this compound has not been isolated in the pure state, but the amino-group must be present in the ϵ -position (*Ber.*, 1911, 44, 132; 1912, 45, 3763). The reducing group and the α -hydroxyl group are thus unsubstituted, as indicated above.

saturated with ammonia, and the solutions set aside for three months. The deposition of the crystalline product commenced in about thirty days, and only material which separated spontaneously in this manner was used in our work. The condensation takes place very slowly, although, curiously enough, the similar reaction between ammonia and galactose is comparatively rapid, and, judging from the polarimetric results obtained, is complete in three days.

Glucoseimine shows very slight mutarotation in water, but this seems due to the speed with which equilibrium is established. Moreover, the compound is partly decomposed when attempts are made to isolate mutarotatory forms by any process of crystallisation, and thus the material has to be used in the form in which it separates during its preparation. A specimen was, however, preserved in a sealed tube in the dark for a year, in the hope that the transformation $\beta \rightarrow \alpha$ would proceed slowly in the solid state. The following polarimetric results were then obtained:

Solvent.	c .	Specific rotation.
Water	1.882	+19.4 \rightarrow 22.1 (constant for 12 hours)
"	4.605	16.7 \rightarrow 22.6 (" " ")
Aqueous methyl alcohol	1.932	20.4 \rightarrow 21.2 (" " 48 ")
Aqueous pyridine	4.636	18.4 \rightarrow 21.8 (" " ")

Equilibrium was very quickly established in each case, and the end values recorded gradually altered owing to decomposition.

Action of Ammonia on Methyl-alcoholic Solutions of Sugar Derivatives.

The following experiments were undertaken for reasons given in the introduction.

Sucrose.

Fifteen grams of dry sucrose were shaken with 200 c.c. of methyl alcohol previously saturated with ammonia. The activity ($\alpha + 9.03^\circ$ for $l=2$) remained constant for forty days and subsequently sucrose separated gradually during a period of eight months. The mother liquor contained the unaltered sugar, and no nitrogen compounds were detected.

α -Methylglucoside.

A solution of 50 grams of α -methylglucoside in 400 c.c. of methyl alcohol saturated with ammonia, maintained a constant rotation for five days, after which the solution deposited the glucoside in large prisms. This interrupted the polarimetric record, but, at intervals during eight months, the crystalline crops were removed, and in each case found to consist of the unaltered glucoside.

Tetramethyl Methylglucoside.

The proportions used were exactly the same as those given above. The specific rotation of the solution remained quite unaffected during several weeks, and the material was recovered unaltered.

Gluconolactone.

10.6 Grams of pure crystalline gluconolactone were dissolved in 120 c.c. of concentrated aqueous ammonium hydroxide ($D_{20} 0.880$), and the solution kept in a vacuum desiccator until all the solvent had been removed. The solid, crystalline residue was drained on porous porcelain, and purified by solution in the minimum amount of water at 60° and fractional precipitation with absolute alcohol. The first material to separate consisted almost entirely of ammonium gluconate, mixed, however, with gluconamide, which also constituted the bulk of the more soluble crops. By frequent repetition of the method of purification, a fairly complete separation of the two products was obtained, but the process was extremely tedious, and was complicated by the ready transformation of the acid amide into the ammonium salt.

Ammonium gluconate crystallises in flat prisms, which decompose at 154° , and show in aqueous solution $[\alpha]_D + 14.5^\circ$ for $c=5$.

Found, $C=33.57$; $H=7.40$; $N=6.76$.

$C_6H_{11}O_7 \cdot NH_4$ requires $C=33.80$; $H=7.10$; $N=6.57$ per cent.

All attempts to convert the salt into the acid amide were unsuccessful.

Gluconamide also crystallises in prisms, which decompose at 28° , with the evolution of gas. The specific rotation in aqueous solution was $[\alpha]_D + 20.24^\circ$ ($c=5$), but this value is not permanent owing to the addition of water. The purest specimen of the compound obtained still contained a small quantity of the ammonium salt (Found, $C=36.08$; $H=6.82$. $C_6H_{13}O_6N$ requires $C=36.92$; $H=6.72$ per cent.).

It should be stated that an attempt to repeat the above reaction, using larger quantities of material, gave only the ammonium salt and no trace of the acid amide. This was doubtless due to the prolonged evaporation of the solvent.

Action of Ethylamine on Glucose.

The action of a cold alcoholic solution of ethylamine on glucose results in an equilibrium being established between the constituents and the condensation product. Twenty-four grams of glucose (1 mol.) were dissolved by shaking with 1 litre of absolute ethyl

alcohol containing 12 grams of ethylamine (2 mols.) The optical activity of the solution rapidly diminished, and, after nine days, a constant levorotation was recorded. The condensation was nevertheless incomplete, and the reaction was therefore continued for four months, after which the solvent was removed in a vacuum. The residue crystallised readily, but showed a marked tendency to become gelatinous during filtration. On the basis of analysis, the polarimetric effect of hydrolysis, and titration of the ethylamine thus liberated, it was shown that the product, although apparently homogeneous, contained about 30 per cent. of unaltered glucose. The preparation, however, yielded crystalline nuclei which were of use in the isolation of the pure compound by the following method.

Glucose (1 mol.) was dissolved by shaking with anhydrous ethylamine (3 mols.). The solution rapidly set to a clear, transparent jelly. A small quantity of absolute alcohol was then added, and the mixture vigorously shaken with a nucleus obtained as described above. The jelly was thus resolved into a crystalline mass, which proved to be the desired condensation product in a state of purity. The yield was nearly quantitative. Analysis of a specimen dried at 60°/15 mm. gave:

C=46.46; H=8.34; N=6.62.

$C_8H_{17}O_5N$ requires C=46.32; H=8.21; N=6.76 per cent.

Ethylaminoglucose crystallises in pointed prisms, melting and decomposing at 107—108°. The compound is hydrolysed by water in the cold, and therefore reduces Fehling's solution, and reacts alkaline. The alcoholic solution, in the absence of moisture, is neutral to litmus, and is only slowly decomposed at the boiling point. The following mutarotation was detected in ethyl-alcoholic solution:

	$[\alpha]_D$		$[\alpha]_D$
$c=0.8416$	-21.98°	→	-12.48
$c=0.7701$	-28.56	→	-12.34

This optical change, which was complete in one hour, was not due to partial hydrolysis promoted by the presence of moisture in the alcohol, as dilution to half the concentration with the same solvent had practically no effect on the activity, even after heating the solution to 66° for four hours in a thermostat.

This result is significant, as similar treatment with 50 per cent. alcohol resulted in complete hydrolysis, the specific rotation, calculated on the weight of glucose formed, then altering to +52.2°. The stability of the iminoglucoside, when heated with anhydrous alcohol, also affords an index of the mechanism of biase formation from glucoseimine.

Formation of By-products in the Condensation.—When the

reaction was carried out in alcoholic solution, the solvent acquired a strong odour resembling that of pyridine. This by-product was volatile, and was obtained, along with the excess of alkylamine, in the alcohol recovered by distillation. The liquid was neutralised with *N*/2-hydrogen chloride, and the liquid again distilled at 50°/20 mm. The crystalline residue consisted of ethylamine hydrochloride, and the distillate once more contained the unknown base in the free state. Hydrochloric acid was then added until the odour of pyridine disappeared, and the solution evaporated to dryness on a water-bath. A very small crystalline residue of the ethylamine salt remained, and presumably the salt of the base had undergone dissociation and subsequent volatilisation.

Action of Ammonia on Fructose in Methyl-Alcoholic Solution.

Finely powdered fructose (50 grams) was dissolved by shaking with 300 c.c. of methyl alcohol previously saturated with ammonia. The filtered solution was preserved in a well-stoppered bottle, and kept in the dark for thirty-three days. During this time the liquid gradually acquired a brown colour, crystals were deposited on the sides of the bottle, and the optical activity of the solution steadily diminished until the liquid was quite inactive.

The solid product was proved by analysis, determination of the specific rotation (-78.7° in water), and conversion into the acetyl derivative (m. p. 170°) to be the substance $C_{12}H_{20}O_8N_2$, isolated by Lobry de Bruyn in a similar reaction.

The mother liquor, which yielded the above compound, was preserved in the dark for an additional nine months, during which time it remained quite inactive. On removal of the solvent in a vacuum, a brown syrup was obtained, which solidified to a glass. This, when dissolved in a small quantity of methyl alcohol and precipitated by the addition of ether, gave a yellow, amorphous, somewhat deliquescent solid. Repeated precipitation effected the removal of the colouring matter and the deliquescent impurities, and, after drying in a vacuum at 60° , *fructoseazine* was isolated as a white powder, which decomposed, after preliminary softening, at 125° . The solubilities resembled those of fructose:

Found, C=44.85; H=5.88; N=9.10.

$C_6H_6O_4N$ requires C=45.28; H=5.66; N=8.80 per cent.

The compound was quite inactive in aqueous solution, even after heating for one hour at 50° with 2 per cent. hydrochloric acid. It reduced Fehling's solution on warming, and gave off ammonia when heated with sodium hydroxide. No ammonia was, however, liberated on heating with either methyl or ethyl alcohol.

The compound did not give the carbylamine test, and the absence of the amino-group was confirmed by the negative result obtained on treatment with nitrous acid. When heated with phenylhydrazine and acetic acid, phenylglucosazone was produced in excellent yield. This was identified by the melting point ($204-205^{\circ}$) and by the specific rotation in acetic acid solution ($[\alpha]_D -80.3^{\circ}$).

The formation and constitution of this derivative of fructose is discussed in the introduction.

Condensation of Glucose with Diethylamine.

Owing to its instability, the product of this reaction could not be isolated in the pure state. The anhydrous sugar (1 mol.) was added to a 33 per cent. solution of diethylamine (2 mols.) in ethyl alcohol, and the mixture shaken at intervals during a period of several weeks. The glucose passed slowly into solution, and the optical activity of the liquid gradually diminished and finally became constant. After removal of the solvent in a vacuum, a clear syrup was obtained, which analysis showed to be a mixture of the condensation product and glucose. The total product was accordingly dissolved in a large excess of ethyl alcohol containing 50 per cent. of diethylamine and kept at 20° for twenty days. During this time the activity again diminished, and again became constant. The solvent and excess of the base were removed in a vacuum. The syrupy residue was now freely soluble in anhydrous diethylamine, and a 20 per cent. solution in this solvent was accordingly preserved for ten days, after which the reagent was removed in a vacuum, and the residual syrup purified by solution in alcohol and precipitation with ether until the washings were no longer alkaline. The gelatinous product was then drained on porous porcelain, but as the use of recrystallising media rendered the mass syrupy, no further purification was possible. Owing to the instability of the compound, the analyses had to be carried out without delay, and the results for carbon and hydrogen were only approximate (Found, $N=5.71$; $C_{10}H_{21}O_5N$ requires $N=5.95$ per cent.). The compound is rapidly decomposed by water, and reduces Fehling's solution, diethylamine being liberated during the process. The specific rotation in methyl-alcoholic solution ($c=1.911$) was $+11.5^{\circ}$, but this value rapidly altered, and can only be regarded as approximate.

Condensation of Glucose with Dimethylamine: Formation of Dimethylaminoglucose.

Sixteen grams of glucose (1 mol.) were fixed with 700 c.c. of absolute methyl alcohol containing 8 grams of dimethylamine (2 mols.), and the mixture shaken at intervals during four months. On filtration and removal of the solvent at 30°/20 mm., a clear syrup remained, which crystallised incompletely. The total product was redissolved in alcoholic dimethylamine, and the above treatment repeated until no further alteration in rotatory power took place. The syrup ultimately obtained, in solubility and behaviour towards reagents, resembled diethylaminoglucose. Analysis of a specimen dried over phosphoric oxide gave:

C=46.05; H=8.17.

$C_8H_{17}O_5N$ requires C=46.37; H=8.21 per cent.

The use of trimethylamine, in an experiment duplicate in every other respect to that described above, gave a solution which showed no alteration in rotatory power when kept for five months. The glucose was, moreover, recovered unaltered, and no derivative containing nitrogen was detected.

Negative results were also obtained in attempts to condense glucose with diphenylamine, acetanilide, or methylanilide.

The authors are indebted to the Carnegie Trust for a research grant in aid of the investigation.

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XXVIII.—*The Form of Extinction Curves: Cobalt Nitrate Solutions.*

By THOMAS RALPH MERTON, B.Sc.(Oxon.).

The emission spectra the distribution of intensity in spectral lines has been the subject of numerous investigations, and has in many cases been found to conform with definite laws. In the case of absorption spectra, however, no attempt appears to have been made to express the shape of extinction curves according to any law, largely, no doubt, on account of the large number of apparently anomalous shapes in which they occur. It has been shown by the

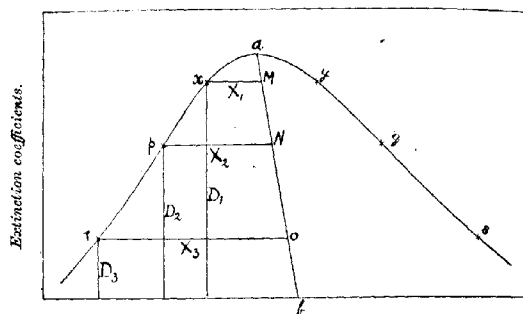
author (*Proc. Roy. Soc.*, 1912, A, **87**, 138) that the superposition of two or more extinction curves may account for the form of apparently complicated curves. It would seem, in fact, simpler to assume that all apparently complicated curves are in reality due to the superposition of curves of simple form than to attempt to express them by any mathematical laws.

The object of the present investigation has been to find some solution which exhibits a single absorption band unaffected by the presence of other superposed bands, and to examine the form of the extinction curve.

An instance of this kind has been found to occur in the case of solutions of cobalt nitrate, which have a single absorption band in the visible spectrum.

The method of investigation and the apparatus used has been described in a previous communication (this vol., p. 124).

FIG. 1.
Wave-lengths.



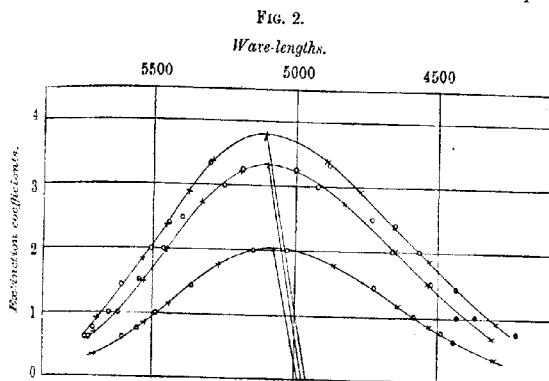
The *D*-lines of a sodium flame were superposed on each absorption spectrum, and the wave-lengths were calculated by means of a carefully drawn interpolation curve. It was found that the standard density plate used showed slightly diminished density below wave-length 4100. As a precaution, no measurements were made below 4250. Kahlbaum's nickel-free cobalt nitrate was used. It was partly dehydrated over calcium chloride in a vacuum, and the amount of cobalt in it was estimated.

It has been found that the form of the absorption curve can be expressed within the limits of experimental error in a simple mathematical form. The manner in which this has been arrived at can best be understood by reference to Fig. 1. The curve given indicates the general form of the extinction curve of a solution of cobalt

nitrate. The curve is found to be symmetrical about the straight line ab , drawn from the maximum through the points M , N , and O , which are found by bisecting the distances $x y$, $p q$, and $r s$ (these being any points of equal extinction on opposite sides of the absorption band).

It has been found that the form of the curve about the line ab may be expressed by the formula $-\log y = c^2 x^2$, where y is any density (D_1 , D_2 , and D_3) relative to the density at the maximum, x the corresponding distance from the line ab (X_1 , X_2 , X_3), and c^2 a constant depending on the nature of the substance. This formula has been found to hold for cobalt nitrate solutions within the limits of experimental error.

In Fig. 2 are given curves of the extinctions of three aqueous



solutions. The circles indicate the determined points, and the crosses the values calculated by the formula.

It will be seen that the points calculated are in good agreement with the values found. Attention must be drawn to the fact that the constant c^2 is not independent of the concentration, but becomes greater as the solution is diluted, that is to say, the band becomes narrower. The magnitude of this can be best appreciated by calculating the "half-widths" of the bands, that is to say, the values of x when $y=0.5$. The concentrations, together with the values of c^2 , the half-widths, and extinction coefficients at the maximum, were as follows:

Concentration, grams of cobalt per litre (approximate).	c^2 .	Extinction coefficient (at maximum).	Half-width.
22	1.523	2.04	444
37	1.405	3.35	463
42	1.262	3.8	488

(For convenience of calculation the values of x were measured in units of 1000 Å.U.)

The fact that the solution does not obey Beer's law is indicated by the fact that c^2 alters with the concentration, and also that the lines about which the curves are symmetrical do not meet at a common point at zero extinction. The points at which these lines cut the axis are, of course, obtained by extrapolation, and in consequence great weight must not be attached to their exact values, but attention may be drawn to the fact that the point appears to move towards the violet with increasing concentration, whilst the wave-length of the maximum moves towards the red.

Measurements of the extinction curves in alcohol solutions indicate that the formula gives as good results in the solvent as in aqueous solutions. It may be pointed out that the expression is not entirely empirical, this form of equation having been used by Michelson and others to express the distribution of light in emission lines. No explanation, however, can be offered for the inclination of the line about which the curve is symmetrical. It seems very probable that curves of this type will be found for many other substances, and it is suggested that this may be the normal form of a single absorption band, most bands being due to the superposition of curves of this type.

Some evidence at least may be looked for in the changes of the constants of the equation in different solvents, and with changes of temperature, and experiments in this direction are now in progress.

25, GILBERT STREET,
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XXIX.—*The Influence of Water on the Partial Pressures of Hydrogen Chloride above its Alcoholic Solutions.*

By WILLIAM JACOB JONES, ARTHUR LAPWORTH, and
HERBERT MUSCHAMP LINGFORD.

PREVIOUS communications dealing with certain properties of hydrogen chloride in alcoholic solution (T., 1908, **93**, 2187; 1910, **97**, 19; 1911, **99**, 917, 1427, 2242) have dealt with the experimental evidence which shows conclusively that, when small quantities of water are added to such solutions, the chemical activity of the hydrogen chloride is greatly depressed; it was also shown that this effect cannot be distinguished in kind from that produced

by the addition of a very weak anhydro-base, such as an amino-compound, to an aqueous solution of hydrogen chloride in water.

The substantial agreement between the quantitative results obtained by several entirely different experimental methods of attack offers support for the solvate theory of acids, which appears far more definite and satisfactory than the data which led Thomsen to formulate that theory (*Thermochemische Untersuchungen*, ii, 430-444; compare also *Thermochemistry*, Ramsay's Text Books of Physical Chemistry, pp. 88 and 81), or the varied considerations which have led many other chemists at various times to adopt the theory in one modification or another (compare, for example, A. Werner, *New Ideas on Inorganic Chemistry*, Hedley's Translation, 1911, p. 210 *et seq.*).

Apart altogether from the chemical interpretation of the results, the data now available establish the view that the thermodynamic potential of hydrogen chloride dissolved in absolute alcohol is depressed by the addition of water, and that to this depression may be traced:

(i) The anticatalytic effect of water in esterification (Goldschmidt), the decomposition of ethyl diazoacetate (Bredig), and other catalytic processes in which the alcohol itself takes a direct part (compare, for example, Reid, *Amer. Chem. J.*, 1909, **41**, 499 *et seq.* In this connexion, also, Acree, *ibid.*, 471; Lapworth and Partington, T., 1910, **97**, 33; Hardman and Lapworth, *ibid.*, 1911, **99**, 2246).

(ii) The anticatalytic effect of water on acid catalysis during reactions in which the alcohol plays no direct part (Lapworth, T., 1908, **93**, 2188, 2189; Dawson, *ibid.*, 1911, **99**, 1).

(iii) The hydrolytic effect of water on salts of weak bases in alcoholic solution (T., 1908, **93**, 2198; 1910, **97**, 19 *et seq.*, and 217 *et seq.*)

(iv) The reduction caused by water on the electromotive force of the hydrogen electrode in alcoholic hydrogen chloride.

Many of the foregoing methods lead to results which are more or less comparable, but only if used in solutions to which the term "dilute" might reasonably be applied, and in such instances as the influence of the non-ionised part of the acid or its non-ionised salts may clearly be either distinguished from that of the ionised acid or neglected.

Other methods of detecting changes in the thermodynamic potential of dissolved substances are those depending on measurements of vapour tensions of solvent or solute, and the intimately associated phenomena of the osmotic pressures and the cryoscopic and ebullioscopic behaviour of the solutions. Of these, the last

three are difficult of application to the particular case of alcoholic hydrogen chloride for fairly obvious reasons, but these reasons do not apply so forcibly to determinations of the partial vapour tension of the hydrogen chloride.

Methods of measuring partial pressures of volatile constituents of liquid mixtures have been worked out with success by numerous investigators, including Gahl (*Zeitsch. physikal. Chem.*, 1900, **33**, 178), Abegg and Riesenfeld (*ibid.*, 1902, **40**, 84), Konowalov (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 910), Perman (*T.*, 1901, **79**, 718; 1903, **83**, 1168), Gaus (*Zeitsch. anorg. Chem.*, 1900, **25**, 236), and McLauchlan (*Zeitsch. physikal. Chem.*, 1903, **44**, 600).

Perman and Price (*Trans. Faraday Soc.*, 1912, **8**, i, 1) have recently made a very successful and simple application of the bubbling method for measurements of the vapour pressures of concentrated aqueous solutions, and found that saturation of the air used for aspiration was attained with remarkable ease. For that case, however, the pressures to be estimated were considerable, while in the cases with which the present authors are dealing, the partial pressures are frequently relatively minute, and prolonged contact of the gas with the liquid is obviously a necessary condition. In the present series of experiments, saturators of the type devised by Gahl were employed where the time taken for any bubble of gas to pass from the bottom of the spiral to the top was at least eight seconds, and these saturators appeared to be quite efficient, as the results were independent of the speed of bubbling.

The volume of gas bubbled through the solutions was determined by passing it first of all through absolute alcohol and determining the weight of this liquid carried away. The gas subsequently entered the solution under examination, and was finally scrubbed with distilled water; the weight of hydrochloric acid carried over was subsequently determined by titration with accurately standardised barium hydroxide.

The device of passing the gas through the liquids in the order mentioned has something of novelty, and has the great recommendation that the composition of the liquid under examination, namely, that in the second vessel (the effective volume of which was about 150 c.c.), remains as nearly as possible constant even after prolonged aspiration. The principle may prove useful in other instances.

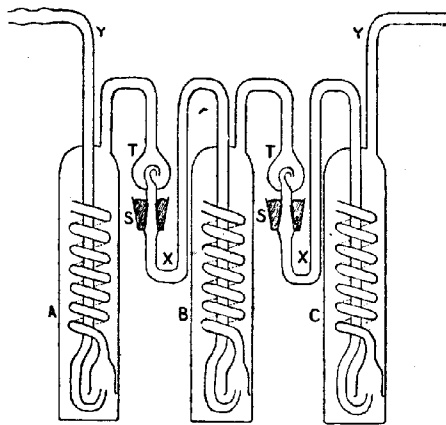
The three vessels were constructed wholly of glass and joined together in the manner indicated in the appended figure.

The saturators, which were originally much as shown, but without the bulb-traps, *T*, *T*, were united by ground glass joints, *S*, *S*, with mercury seals, and when set up the combination could be

immersed completely in the water of a thermostat at $25^{\circ} \pm 0.05$, so that only the vertical end-pieces, *Y, Y*, emerged.

In certain cases it was found at the end of an experiment that drops of liquid were present in the lower parts, *X, X*, of the bent tubes joining the vessels; as it was thought possible that this might be the result of spraying, the bulb-traps, *T, T*, were added. It was found that no detectable quantity of liquid was deposited in these, so that the deposition was in all cases due to a slight condensation of the vapour as the result of slight cooling in the upper portion of these tubes near the surface of the water. This phenomenon could not appreciably affect the results obtained, as all the vaporised alcohol from *A* passed into *B*, whilst the slight deposition in the entry tube of *B* was compensated for by the removal from *B* of the amount deposited, by resaturation of the gas

FIG. 1.



in the main bulk of liquid in this vessel, and the whole of the hydrogen chloride carried over from *B* was carried into *C*, and there retained. The gas, after passing through *C*, was always passed through a shallow layer of water in a subsidiary wash-bottle, but invariably proved to be free from all detectable traces of hydrogen chloride. The pressure of the gas escaping from the third vessel was therefore practically identical with that of the atmosphere at the time of the experiment. The dehydrated alcohol used was prepared from commercial absolute alcohol by boiling with calcium turnings until a portion of the clear liquid set to a jelly on addition of a few drops of water (compare *T.*, 1910, 97, 24), when it was

distilled, the first and last portions being rejected. The alcohol obtained had D_4^{20} 0.78493 without reduction to vacuum. Squibbs (Landolt-Börnstein, "Tabellen," p. 360) gave the value 0.78496, and Mendeléeff 0.78522 (*ibid.*, p. 359).

For the preparation of the moist alcohols used, either this material or, in one or two cases, carefully redistilled commercial absolute alcohol was used and mixed with distilled water, the percentage of water present being checked in each case by determination of the density.

The hydrogen chloride solutions were prepared by passing the carefully dried gas into the alcohol contained in a vessel which was cooled by immersion in a stream of cold water, and their precise compositions subsequently checked by titration against carefully standardised barium hydroxide solution and by density determinations.

All solutions were used very shortly after preparation, and were prepared and preserved in vessels made wholly of glass, from which they were transferred to the aspiration apparatus without exposure to the air.

Hydrogen was used as the gas for aspiration, and was generated by the action of purified zinc on dilute hydrochloric acid, and was passed successively through dilute potassium hydroxide solution, 10 per cent. silver nitrate solution, 30 per cent. potassium hydroxide solution, and pure sulphuric acid, then over dry potassium hydroxide (in sticks), and finally phosphoric oxide. Immediately before entering the first aspiration vessel the purified hydrogen was brought to the temperature of the thermostat by passing it through a glass spiral immersed in the bath.

In preliminary experiments, air, instead of hydrogen, had been used, but it was found that the values of the partial pressure for a given solution thus determined fell nearly in direct proportion to the volume of air passed through the solution; it may be added however, that the value of the partial pressure obtained by extrapolation to the value zero for the volume of air used was, within the limits of experimental error, identical with the almost unvarying value obtained with hydrogen. Some colour always developed in the solution when air was used, and yellow drops appeared in the tubes joining the three sections of the apparatus; these signs of chemical change were entirely absent when hydrogen was employed.

Calculation of Partial Pressures from Experimental Results.

If M was the mean atmospheric pressure in mm. of mercury during an experiment, then $M + 20$ represented with sufficient

accuracy the pressure of the mixed alcohol vapour and hydrogen leaving the vessel *A*, and $M+11$ the pressure of mixed gases leaving the vessel *B*.

The vapour pressure of ethyl alcohol at 25° is 59.5 mm. (Ramsay and Young, *Phil. Trans.*, 1886, 177, 155), so that, if the gases and liquid are in equilibrium in the space at the top of *A*,

$$\frac{59.5}{M+20} = \frac{\text{Vol. of alcohol vapour}}{\text{Vol. of H}_2 + \text{vol. of alcohol vapour}}.$$

If W was the weight of alcohol evaporated from *A*, and its vapour density is normal at 25° and 59.5 mm., then the volume which the alcohol vapour would occupy if undiluted was:

$$\frac{W \times 22410 \times 298 \times 760}{46.05 \times 273 \times (M+20)} \text{ c.c.}$$

It follows that the total volume of hydrogen and alcohol vapour was:

$$\frac{W \times 22410 \times 298 \times 760}{59.5 \times 46.05 \times 273} \text{ c.c.,}$$

the partial pressure of the hydrogen chloride in the solution being given by

$$P = \text{total pressure in } B \times \frac{\text{Vol. of gaseous HCl removed}}{\text{Total volume of gas passing out of } B}.$$

When q was the titre of hydrogen chloride removed from the second vessel in terms of $N/10$ -alkali, then the volume of hydrogen chloride which had escaped from the second vessel was:

$$\frac{q \times 22410 \times 298 \times 760}{10^3 \times 273 \times (M+11)}.$$

Introducing this in the previous expression and simplifying, the following relation is obtained:

$$P = \frac{274q \times (M+11)}{10^3 W \times (M+20) + 274q}.$$

The question of the influence of change in the concentration of the hydrogen chloride during the course of an experiment has carefully been considered, but the decrease in quantity of the hydrogen chloride in the most extreme case, namely, experiment No. 5 on the list given later, did not amount to more than 0.5 per cent. of the whole, and the change in the amount of water present must have been even smaller; the alteration in the quantity of alcohol in the middle vessel due to its slightly lower partial pressure is partly compensated for by the increasing volume of gas due to expansion under decreasing pressure, and was also almost inappreciable in comparison with other experimental disturbances. The view that these factors are almost negligible is confirmed by comparison of the partial pressures as determined

from experiments of varying duration, such as No. 4 contrasted with 5, 9 with 10, or 19 with 21. No correction for such disturbances has therefore been applied.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
1	0.78493	0.86405	3.188	0.000	3.135	54.66	759	1.3	4.69	} 4.69
2	0.78493	0.86405	3.188	0.000	3.443	59.94	759	1.3	4.68	
3	0.78882	0.86599	3.181	0.529	2.458	39.54	753	1.8	4.35	} 4.29
4	0.79306	0.86988	3.191	1.132	1.954	28.00	754	0.9	3.86	
5	0.79306	0.86988	3.191	1.132	4.357	61.58	753	1.1	3.81	} 3.90
6	0.79841	0.87357	3.188	1.891	1.636	18.85	768	0.6	3.11	
7	0.80207	0.87643	3.195	2.452	4.996	46.34	759	1.8	2.50	} 2.58
8	0.80207	0.87643	3.195	2.452	5.748	54.63	759	2.3	2.56	
9	as in 1	—	2.390	0.000	1.386	13.62	756	0.5	2.65	} 2.62
10	as in 1	—	2.390	0.000	2.811	27.09	756	0.9	2.60	
11	as in 3	0.84952	2.395	0.537	3.705	30.85	760	1.3	2.25	} 2.25
12	as in 4	0.85257	2.392	1.150	1.307	8.39	750	1.0	1.74	
13	as in 4	0.85257	2.392	1.150	2.849	18.23	750	1.2	1.73	} 1.76
14	as in 6	0.85422	2.392	1.920	5.892	25.93	765	2.4	1.19	
15	as in 1	0.81716	1.168	0.000	4.663	13.88	751	1.0	0.806	} 0.81
16	as in 1	0.81716	1.168	0.000	4.960	14.94	751	0.8	0.815	
17	0.78701	0.81968	1.171	0.285	7.245	16.98	744	2.5	0.634	} 0.66
18	0.78701	0.81968	1.171	0.285	10.310	24.14	745	1.6	0.633	
19	as in 3	0.82009	1.165	0.548	3.198	6.01	762	0.9	0.506	} 0.52
20	as in 3	0.82009	1.165	0.548	5.903	11.11	762	0.9	0.509	
21	as in 3	0.82009	1.165	0.548	8.401	15.71	763	0.8	0.506	} 0.52
22	as in 4	0.82304	1.170	1.173	4.964	4.41	757	1.9	0.241	
23	as in 1	—	0.751	0.000	4.106	6.35	760	1.5	0.419	} 0.42
24	as in 1	—	0.751	0.000	5.061	7.74	760	1.6	0.414	
25	0.78900	0.80979	0.752	0.579	4.809	2.81	759	1.8	0.158	} 0.22
26	0.78900	0.80979	0.752	0.579	5.251	3.07	759	1.8	0.158	
27	as in 1	0.79049	0.275	0.000	3.202	1.23	764	0.6	0.104	} 0.11
28	as in 1	0.79049	0.275	0.000	6.232	2.55	764	0.7	0.111	
29	as in 17	0.79439	0.274	0.288	5.058	0.67	761	1.6	0.039	} 0.06
30	as in 17	0.79439	0.274	0.288	5.849	0.79	760	1.4	0.037	

The experimental data, with the deduced partial pressures of hydrogen chloride, are summarised in the preceding table, where are given:

Under column I, the reference number of the experiments.

Under column II, the values of D_v^{25} (without correction to vacuum) for the samples of anhydrous or moist alcohols from which the solutions of hydrogen chloride were prepared.

Under column III, the values of D_v^{25} for the hydrogen chloride solutions.

Under column IV, the numbers of gram-molecules of hydrogen chloride per litre initially present in the solution in *B*.

Under column V, the numbers of gram-molecules of water per litre present in the solution in *B*.

Under column VI, the values of *W*, or weight of alcohol (corrected to vacuum) evaporated from the vessel *A*.

Under column VII, the values of *q*, or the titres of hydrogen chloride removed from the second vessel in c.c. of *N*/10-alkali.

Under column VIII, the values of M , the mean atmospheric pressure in mm., if necessary, prevailing during the aspiration.

Under column IX, the mean rates of bubbling in litres of gas per hour.

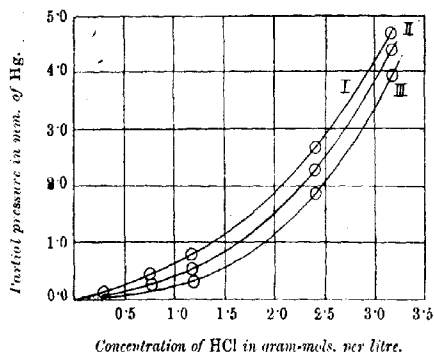
Under column X, the deduced partial pressures of hydrogen chloride in mm. of mercury.

Under column XI, the values of P calculated by means of the formula given on p. 262.

The discrepancies between parallel experiments indicate agreement within 0.06 mm., or about 2.5 per cent., for pressures of 2.50 mm. or more; for lower pressures the margin of discrepancy in the absolute values is still smaller, although the percentage error becomes greater; the lowest pressures agree with one another within less than 0.01 mm.

There is, however, good reason to distrust the very lowest values

FIG. 2.



found in moist alcohol, namely, those obtained in experiments 25 or 26, and 29 or 30. These, although concordant amongst themselves, appear anomalous when contrasted with the others by any method, graphic* or formal; the numbers in column XI are probably much nearer the true values than those found experimentally. Careful repetition of the experiments 25 and 26 gave results practically identical with those in column X, and as the very lowest value in the case of absolute alcoholic solution (experiments 27 and 28) appears quite normal, it appears most likely that for some reason the experimental method, when applied to solutions with such small concentrations of hydrogen chloride in

* This is best seen by plotting the logarithms of the partial pressures against logarithms of the concentration of hydrogen chloride.

moist alcohol, gives abnormally low results. On the other hand, it is possible, though improbable, that the depression caused by very small quantities of water increases much more rapidly at these low concentrations of hydrogen chloride than the other results would suggest.

In Fig. 2 are given curves indicating the manner in which the partial pressure of the hydrogen chloride varies with the concentration of this gas in alcohol containing a fixed quantity of water.

Curve I refers to anhydrous solutions.

Curve II refers to solutions containing 0.5 gram-mol. H_2O per litre.

Curve III refers to solutions containing 1.0 gram-mol. H_2O per litre.

It may be noted, on comparing the different quantities of water which correspond with the same partial pressures, that, at 4 to 5 mm., 1 gram-molecule of water has the apparent effect of removing $\frac{1}{4}$ gram-molecule of hydrogen chloride from the sphere of action; at 1.5 mm. or less, the proportion apparently removed is about $\frac{1}{2}$ gram-molecule over a considerable range.

In Fig. 3 are given curves showing the influence of varying quantities of water on the partial pressures of hydrogen chloride when the concentration of the latter is fixed. The relative depression caused by a given quantity of water is seen to increase markedly as the concentration of the hydrogen chloride diminishes.

Values of Partial Pressure of Hydrogen Chloride in Anhydrous Alcohol.

In endeavouring to find an expression adequately to represent the relation between partial pressures and concentrations of hydrogen chloride and alcohol vapour, use was made of Duhem's differential equation:

$$\frac{d \cdot \log p}{dx} + x \frac{d \cdot \log P}{dx} = 0,$$

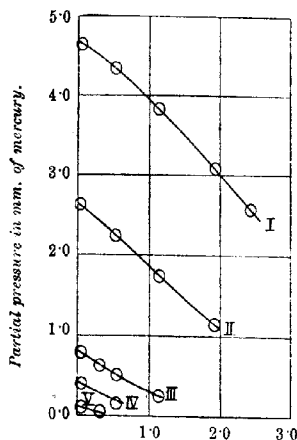
where P here represents the partial pressure of the hydrogen chloride, p that of the alcohol, and x the number of gram-molecules of hydrogen chloride per gram-molecule of alcohol in the liquid phase.

Dolezalek applied this formula to the case of aqueous hydrogen chloride on the assumption that $\log p$ was a linear function of x . Integration led to the equation $\log P = a \log x + k$, where a and k are constants, and the calculated values over a range from $P=0.52$ to 277 were fairly consistent with the experimental values only within

a margin of about 15 per cent. (*Ber. Deut. physikal. Ges.*, 1903, 5, 4). In the case of alcoholic hydrogen chloride, a similar degree of concordance is noticed, but when consideration is paid to the fact that saturated hydrogen chloride in alcohol is between 10 and

FIG. 3.

Curve I.	HCl=3.19	gram-molecules per litre
" II.	HCl=2.39	" " "
" III.	HCl=1.17	" " "
" IV.	HCl=0.75	" " "
" V.	HCl=0.275	" " "



Concentration of H₂O in gram-molecules per litre.

11.V by volume, it becomes clear that the algebraic expression equated to $\frac{d \cdot \log p}{dx}$ must contain a power of x not less than the second.

Putting

$$\frac{d \cdot \log p}{dx} = a' + b'x + d'x^2,$$

and placing this in Duhem's equation, we obtain an equation of the type:

$$\log P = a_0 \log x + b_0 x + d_0 x^2 + k_0,$$

where four constants are present. The employment of the term in x^2 would be unnecessary if it were desired to include only the values for anhydrous solutions in the table on p. 258, where its influence is only that of a very small correction term, but its introduction should permit of more accurate extrapolation beyond those limits to both higher and lower values.

In calculating the values of x , the densities at 25° of anhydrous alcohol containing various strengths of hydrogen chloride, as above given, were used; the density of 10.45 volume-normal hydrogen chloride at 25° was found to be 0.96651.

The formula becomes:

$$\log_{10} 10P = 1.284 \log X + 0.01106X + 0.000115X^2 - 0.256,$$

where $X = 100x$.

The following table shows the applicability of this formula:

n^*	x	P (observed).	P ("calc.")
(10.45	0.82	760.0 (nearly)	760.0
3.188	0.1985	4.69	4.63
2.39	0.1451	2.63	2.63
1.168	0.0696	0.811	0.808
0.751	0.0444	0.417	0.423
0.275	0.0162	0.108	0.107

The General Form.

Largely no doubt in virtue of the four "constants," equations of similar type apply when n , the volume-normality of the hydrogen chloride, is used instead of x , its relative molecular concentration. Not only is this the case with the anhydrous solution, but also with solutions containing water; that is, a general equation of the type:

$$\log_{10} \pi = a \log_{10} C + bC + dC^2 + k$$

applies to all solutions when $\pi = 100P$

$$C = 10n.$$

Moreover, the values of the "constants" vary quite regularly with the amount of water, so that each constant may be expressed in terms of w , the number of gram-molecules of water present per litre of solution; thus:

$$a = 1.3171 + 1.0306w + 0.3907w^2.$$

$$10^3b = 3.847 - 12.11w - 3.851w^2.$$

$$10^4d = 1.2633 + 0.398w + 0.10798w^2.$$

$$k = 0.4392 - 1.2481w - 0.5014w^2.$$

These numbers, it may be noted, are intended for use in the neighbourhood of the region covered by the measurement in the table on p. 258. Their application for the calculation at somewhat higher pressures is partly justified by their agreement with the fact that the concentration of alcoholic hydrogen chloride saturated at 25° and atmospheric pressure, is between 10 and 11 normal, by volume, even in presence of small quantities of water. The values for the partial pressures, calculated by means of the above formula,

* n is used to represent the concentration of the hydrogen chloride in gram-molecules per litre.

are given, within 0.01 mm., in column XI of the table on p. 258; the order of agreement is within the limits of experimental error, with the exception possibly of the doubtful cases mentioned on p. 259.

The fact that the method described in the present paper gives satisfactory results only over a range where the concentrations of hydrogen chloride are considerable, prevents any direct comparison of these with previous observations on the influence of water on the properties of alcoholic hydrogen chloride. It is hoped that by an extension of the earlier experiments to higher concentrations of acid such a comparison may prove of considerable theoretical interest, but further discussion may be reserved until more data have been accumulated; the case of electromotive forces of concentration cells containing alcoholic hydrogen chloride will be dealt with specially.

Summary.

(1) The partial pressures of hydrogen chloride in the saturated vapours of alcoholic solutions of this gas have been measured at 25° over a considerable range.

(2) The partial pressures increase very rapidly with the concentration, although much less rapidly than with aqueous solutions.

(3) The partial pressures are reduced very considerably by the presence of small quantities of water, the relative fall increasing as the concentration of hydrogen chloride diminishes.

(4) The formula of Dolezalek applies, in its simplest form, over a very small range only; in an extended form it applies over a wide range, whilst a similar but complicated formula may be used to calculate the influence of change of concentration of either hydrogen chloride or water or both.

The authors beg to acknowledge their indebtedness to the Government Grant Committee of the Royal Society for a grant, from which much of the cost of the investigation was defrayed.

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XXX.—*The Presence of Helium in the Gas from the Interior of an X-Ray Bulb.*

By SIR WILLIAM RAMSAY, K.C.B.

LAST July a brief statement was made in a letter to *Nature* to the effect that the residual gas extractable by heating the glass of an X-ray bulb contained a measurable trace of helium, in which the neon spectrum could also be identified. The object of this note is to describe the experiment in greater detail, and also to state that the result has been confirmed.

In the first experiment the glass of four very deeply coloured X-ray bulbs, furnished me by the kindness of my friend, Sir James Mackenzie Davidson, was placed in a combustion tube of hard glass; junction was made with a Töpler's pump by thick-walled indiarubber tubing, protected from possibility of leakage by a mercury guard-tube. Pure oxygen was admitted to the tube four times, and removed by pumping until a vacuum tube in circuit showed green phosphorescence; in this way all adhering air was removed from the surface of the glass. The temperature of the tube was then raised to redness, and the gases extracted by pumping. This gas was collected in a small tube containing mercury; in order to expel any air from the walls of the tube, the mercury was boiled until no more bubbles of gas escaped; it was then inverted over the end of the capillary tube of the pump. The gas which it contained was sucked into a bulb through an inverted syphon, closed by a ground-on cap, which could be removed below the mercury of the trough; in this way a stopcock is avoided, and leakage is rendered quite impossible. Connected with the bulb was a small bulb containing about 0.2 gram of cocoanut charcoal; the charcoal-bulb had been heated to the temperature of boiling sulphur, and all gas removed by pumping again until green phosphorescence was seen in the attached vacuum-tube. The gas from the glass was then left in contact with the charcoal cooled with liquid air for about half-an-hour, in order that the oxygen might be completely absorbed. The residual gas in the bulb was next made to enter a capillary tube of very narrow bore, furnished with an electrode sealed in at its upper end. This was done by allowing mercury to enter the bulb from below, in the same manner as mercury enters the barrel of a Töpler pump. The mercury in the capillary tube was then frozen with liquid air; there is thus a double advantage: the gas is confined, and the mercury vapour is condensed, so that its spectrum no longer appears in the capillary

tube. The frozen mercury serves, moreover, as one electrode, the other being the platinum wire sealed through the end of the capillary tube.

The volume of the residual gas was not measured on this occasion, but its spectrum showed all the lines of helium with great brilliance, and at the same time some of the more brilliant of the neon red lines were faintly visible.

The second experiment was carried out differently. The exit tube of an X-ray bulb was connected by means of thick-walled rubber tubing with a Töpler pump, a vacuum-tube being as before in circuit. The drawn-out end of the exit tube had previously been scratched with a glass-knife, so that it could be broken through the rubber by the help of pliers. Before this was done, all air was pumped out of the connecting tube, and after the end was broken a guard-tube was slipped over the junction, and filled with mercury; leakage was thus rendered impossible. The X-ray bulb stood in an air-bath of asbestos card, and was heated to about 350° . The phosphorescence of the tell-tale vacuum tube was not altered when connexion was made with the X-ray bulb, but after heating, the spectrum showed oxygen and nitrogen and a trace of carbon dioxide to be present. About a cubic centimetre of pure oxygen was admitted into the X-ray bulb, so as to "wash" it out; the gases collected by means of the pump were treated as already described. The result was the same; the spectrum was that of helium, and only two of the stronger red lines of neon were visible.

The process was repeated with a second and a third X-ray bulb; the result was the same. The volume of the combined gases was measured; it was about 0.39 cubic millimetre.

The bulbs were then broken up, and the powdered glass was placed in a combustion tube connected with the pump with the same precautions against leak as have already been described; the combustion tube was pumped empty, and four times washed out with oxygen; and the gas given off on heating was collected. After treatment with cooled charcoal, not a trace of any gas could be seen when the mercury was run up into the capillary tube; all the gas was absorbable in cooled charcoal. This negative experiment gives strong reason for the conclusion that the inactive gas in the former experiments was not derived from any air which might have leaked in. Indeed, supposing that the 0.39 cubic millimetre of inactive gas had been derived from air, the amount of air required to furnish the helium and neon found, supposing them to have been present in the proportions in which they exist in air, would have been no less than 22 cubic centimetres.

The fact, therefore, has to be accounted for that it is possible to

extract from the interior of an X-ray bulb helium mixed with a trace of neon in measurable quantity. Its source is, of course, a matter for conjecture; it may be that under the influence of the cathode discharge helium and neon are able to penetrate the walls of the bulb, which exclude oxygen and nitrogen. Or it is possible to imagine another explanation less likely to be received without challenge: that these gases are in some way the product of the cathode rays.

LONDON.

XXXI.—*Vaubel's Supposed Phenyl-di-imine.*

By MARTIN ONSLOW FORSTER and JOHN CHARLES WITHERS.

WHILE investigating the reduction of diazoaminobenzene with zinc dust in alkali, Vaubel (*Ber.*, 1900, **33**, 1711) obtained a liquid boiling at 162—164°, appearing to have the composition $C_6H_5N_2$, and regarded by him as phenyl-di-imine, $C_6H_5 \cdot N:NH$.

Our attention was attracted to this substance by two factors, namely, the improbability of its surviving the method of preparation, and the importance of studying such a type supposing it to be capable of existence. We accordingly attempted to prepare phenyl-di-imine by Vaubel's process, which consists in slowly distilling the alcohol from a solution of diazoaminobenzene in alcoholic alkali to which zinc dust has been added, and then passing a current of steam through the residual liquid after acidification.

It is not clear from the meagre details furnished by Vaubel whether acidification was practised on the alkaline liquid alone or on the solid matter suspended in it; we therefore separated the solid in the earlier experiments, but finding that the liquid alone did not give oil when acidified and distilled in steam, we conclude that Vaubel allowed the solid to remain suspended in the alkaline liquid to which dilute sulphuric acid was then added. On following this course, we also obtained a yellow oil which, after being shaken with alkali to remove phenol, was divisible by distillation under 13 mm. pressure into two fractions, boiling at 67—70° and 74—75° respectively, the latter being pure aniline. The more volatile, pale yellow fraction, which should have been phenyl-di-imine, was analysed several times because the empirical formula indicated, namely, $C_{18}H_{17}N_7$, was difficult to reconcile with any probable individual.

Qualitative examination of the substance, however, revealed the

properties of both aniline and phenylazoimide, and we believe, therefore, that the liquid obtained in the manner described is a constant boiling mixture of those two compounds in the proportion $2\text{C}_6\text{H}_5\cdot\text{N}_3 + \text{C}_6\text{H}_5\cdot\text{NH}_2$. This conclusion is confirmed by the fact that on distilling a mixture of phenylazoimide with excess of aniline under the above-mentioned pressure, the lower fraction was a liquid agreeing in every detail, qualitative and quantitative, with the supposed phenyldi-imine which we obtained from diazoaminobenzene.

The fact that Vaubel's product has the composition $\text{C}_6\text{H}_6\text{N}_2$ is explained by the circumstance that, having been distilled under atmospheric pressure, its composition would be different from that of a product fractionated under 13 mm., and it is significant that an equimolecular mixture, $\text{C}_6\text{H}_5\cdot\text{N}_3 + \text{C}_6\text{H}_5\cdot\text{NH}_2$, would have the same percentage composition as phenyldi-imine.

Certain points in Vaubel's description of phenyldi-imine are in agreement with our hypothesis that his material is a mixture of phenylazoimide and aniline. According to his statement, it does not form salts with dilute alkalis, it is dissolved only in part by hydrochloric acid, and with sulphuric acid yields "eine eigenthümliche, weissliche, klebrige Verbindung, die sich aber bald wieder in Oel und Säure scheidet," and which doubtless consists of aniline sulphate impregnated with phenylazoimide. Furthermore, the boiling point of phenyldi-imine under atmospheric pressure was stated to be $162\text{--}164^\circ$, and the only recorded boiling point of phenylazoimide at such a high pressure is $161\text{--}162^\circ/754$ mm. Moreover, the distillation of phenyldi-imine was accompanied by extensive decomposition and the production of a white solid, the composition of which was not determined; it is highly significant that when phenylazoimide is allowed to mix with aniline at 150° , a colourless, solid base, $\text{C}_{12}\text{H}_{12}\text{N}_2$, is produced, accompanied by liberation of nitrogen (Wolff, *Annalen*, 1912, **394**, 59).

It remains to explain how this mixture is produced in the circumstances of Vaubel's experiment. Recalling the fact, already mentioned, that the solid was not removed from the alkaline liquid before acidification, it will be recognised that the supposed phenyldi-imine arose from the action of dilute sulphuric acid on a mixture of zinc dust and diazoaminobenzene. Supposing the acid to resolve the latter into aniline and diazonium salt, a portion of which becomes reduced to phenylhydrazine, this base, in action with diazonium salt, would yield a further quantity of aniline accompanied by phenylazoimide. It might be supposed that on distillation in steam, phenylazoimide would pass over alone, but we find that a faintly acid solution of aniline sulphate will yield a consider-

able proportion of the base when a current of steam is passed continuously through the liquid. The variety of the changes involved in this explanation will readily account for the low yield recorded by Vaubel and confirmed by our own experiments.

EXPERIMENTAL.

Twenty-five grams of diazoaminobenzene, freshly prepared, were dissolved in 100 c.c. of alcohol, and heated with 50 c.c. of 20 per cent. aqueous sodium hydroxide and 20 grams of zinc dust during two hours, in the course of which time there distilled over 125 c.c. of liquid containing aniline and phenylhydrazine. The pale yellow oil remaining in the flask became solid on cooling, and consisted of pure diazoaminobenzene, as stated by Vaubel; this was filtered, and the alkaline filtrate, after extraction with ether, did not give an oil when acidified and distilled in steam. In subsequent experiments, therefore, the zinc and diazoaminobenzene were not removed before sulphuric acid was added, and in these circumstances a pale yellow oil slowly distilled in the steam.

The product accumulated from 225 grams of diazoaminobenzene was dissolved in ether and extracted with sodium hydroxide, from which phenol alone was recovered; on evaporating the ether after drying with sodium sulphate about 15 grams of oil remained, divided by fractional distillation under 13 mm. pressure into 4 grams boiling at 67—70° and 10 grams boiling at 74—75°, the latter consisting of pure aniline. The more volatile portion, which had a distinct odour of phenylazoimide, was redistilled, boiling at 64—65°/13 mm.:

0.1385 gave 0.3300 CO₂ and 0.0623 H₂O. C=64.98; H=5.03.

0.1162 „ 29.0 c.c. N₂ at 15° and 756 mm. N=29.08.

2C₆H₅·N₃ + C₆H₅·NH₂ requires C=65.22; H=5.17;
N=29.61 per cent.

When shaken with dilute hydrochloric acid a portion dissolved, and the solution, when freed from oil by ether, gave with hypochlorite the colour characteristic of aniline, which was also indicated by diazotisation and coupling; the ethereal extract deposited phenylazoimide on evaporation, this effervescing strongly with concentrated sulphuric acid or a solution of stannous chloride in hydrochloric acid. The original substance also gave the intense colour with hypochlorite, and when reduced with stannous chloride gave aniline and nitrogen, unaccompanied by phenylhydrazine, which should be formed if phenyldi-imine were present. With concentrated sulphuric acid vigorous liberation of gas took place:

0.3003 gave with 75 per cent. H_2SO_4 43.4 c.c. N_2 at 20.5° and 764 mm. $\text{N}=16.50$.

$2\text{C}_6\text{H}_5\cdot\text{N}_3 + \text{C}_6\text{H}_5\cdot\text{NH}_2$ requires $2/3$ azidic $\text{N}=16.92$ per cent.

For comparison with this material an artificial mixture of phenylisourea with considerable excess of aniline was distilled under 13 mm. pressure, yielding an early fraction boiling at $62-65^\circ$; this was redistilled and analysed, the percentages of nitrogen and two-thirds the azidic nitrogen being in close agreement with the above, from which it did not differ by any qualitative test.

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XXXII.— $\alpha\delta$ -Derivatives of Adipic and β -Methyladipic Acids, and the Preparation of Muconic and β -Methylmuconic Acids.

By HENRY STEPHEN and CHARLES WEIZMANN.

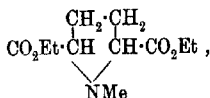
THE experiments on $\alpha\delta$ -derivatives of adipic and β -methyladipic acids, of which a short account has appeared (P., 1912, **28**, 95), have been continued, and have led finally to some interesting results. The work of Markovnikov (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 331), and also the process discovered by the Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 221849), have made adipic and β -methyladipic acids accessible. It was desirable to prepare from these acids, on the one hand, $\alpha\delta$ -diaminoadipic and $\alpha\delta$ -diamino- β -methyladipic acids, and on the other, muconic and β -methylmuconic acids.

Considerable quantities of adipic and β -methyladipic acids have been prepared by oxidising cyclohexanone and 4-methylcyclohexanone respectively with nitric acid (D 1.4), and the acids thus obtained have been brominated.

The bromination of these acids was carried out by the usual Hell-Volhard method, with the difference that thionyl chloride was used for the preparation of the acid chlorides. The use of this reagent leads to the formation of very pure acid chlorides. The product from the bromination was treated with anhydrous formic acid or alcohol according as the free acid or ester was required; and in this way we have prepared the $\alpha\delta$ -dibromo-acids and esters. These dibromo-esters have also been described by Le Sueur (T., 1909, **95**, 273),

The displacement of the two bromine atoms in the above $\alpha\delta$ -dibromo-compounds by the amino-group was found to be a matter of considerable experimental difficulty. The action of ammonia, both aqueous and alcoholic, leads to the formation of pyrrolidinedicarboxylic esters or acids. It was therefore thought that the treatment of the dibromo-esters with potassium phthalimide, and the subsequent hydrolysis of the diphthalimino-compounds might lead to a satisfactory result. This proved to be correct especially in the case of the $\alpha\delta$ -dibromoadipic esters; but the $\alpha\delta$ -dibromo- β -methyladipic esters were found to react with potassium phthalimide with great difficulty, and only small quantities of the diphthalimino-compounds could be obtained.

The preparation of muconic and β -methylmuconic acids by removing two molecules of hydrogen bromide from the corresponding dibromo-esters was also one of considerable difficulty. In this connexion, Willstätter and Lessing (*Ber.*, 1902, **35**, 2065) found that when ethyl $\alpha\delta$ -dibromoadipate was treated with methylamine in benzene solution, ethyl 1-methylpyrrolidine-2:5-dicarboxylate was produced.



Le Sueur (*loc. cit.*) has also observed a similar reaction in an attempt to obtain the unsaturated ester from the same dibromo-ester, by treating the latter with mono- or diethylaniline, obtaining, however, the corresponding *N*-pyrrolidine compounds, analogous to that obtained by Willstätter and Lessing (*loc. cit.*). In our experiments we have studied the action of trimethylamine in alcoholic solution (33 per cent.), and triethylamine in dry benzene, on methyl and ethyl $\alpha\delta$ -dibromoadipates and $\alpha\delta$ -dibromo- β -methyladipate respectively, and have succeeded in isolating the corresponding unsaturated esters which on hydrolysis led to the acids. The yields obtained by these methods are small, due to the same tendency of ring formation, and here again the results obtained are more satisfactory in the case of the dibromo-adipic esters than with the homologue. As a further attempt to obtain the unsaturated compounds, we have treated the dibromo-esters with quinoline, but only very small quantities of unsaturated esters could be isolated.

The diacetoxo-compounds of ethyl $\alpha\delta$ -dibromoadipate and ethyl $\alpha\delta$ -dibromo- β -methyladipate have also been prepared by heating the above esters with fused potassium acetate in glacial acetic acid.

EXPERIMENTAL.

Bromination of Adipic Acid.

In order to brominate the adipic acid obtained as stated above, 100 grams of the acid were treated with 190 grams of thionyl chloride, an excess of 20 per cent. being used. The mixture was warmed on the steam-bath until the whole had assumed the liquid state, and there was no further evolution of hydrogen chloride, which requires about one hour for completion. Pure bromine (240 grams) was then added gradually during a period of forty-eight hours, and the whole continuously heated on the steam-bath until evolution of hydrogen bromide had ceased.

Methyl $\alpha\delta$ -dibromoadipate, $\text{CO}_2\text{Me}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{Me}$.

This ester was obtained by carefully adding methyl alcohol to the bromo-acid chloride prepared above, until the somewhat violent reaction had subsided. On cooling, the bromo-ester was poured into water, extracted several times with ether, the ethereal extract washed with a dilute solution of sodium hydrogen sulphite, and finally several times with water; on removal of the ether a semi-solid mass remained, which was distilled under diminished pressure. The ester (yield, 175 grams from 100 grams of adipic acid) obtained boils at $182^\circ/10$ mm., and is a colourless liquid, which on cooling partly solidifies to a white, crystalline solid.

This, after being separated from the liquid portion by pouring the mixture on a porous plate, was crystallised from ethyl alcohol, and obtained in white needles, which melted at 75° . The ester is soluble in methyl or ethyl alcohols, ether, benzene, or chloroform.

Ethyl $\alpha\delta$ -dibromoadipate, $\text{CO}_2\text{Et}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$.

This was obtained in an analogous way to the methyl ester. It also exhibited the same semi-solid state, and the solid modification of the ester was crystallised from ethyl alcohol and obtained in white needles melting at 65° . The ester distils at $195^\circ/10$ mm.; the solubility was the same as for the methyl ester, and the yield was 180 grams from 100 grams of adipic acid.

 $\alpha\delta$ -Dibromo- β -methyladipic Acid,
 $\text{CO}_2\text{H}\cdot\text{CHBr}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$.

β -Methyladipic acid (160 grams: 1 mol.) was brominated as described above. The bromo-acid chloride was converted into the free acid by the addition of anhydrous formic acid until the reaction

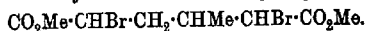
had ceased. A viscid, yellow oil was obtained, from which after several weeks crystals of $\alpha\delta$ -dibromo- β -methyladipic acid separated. When recrystallised from anhydrous formic acid it is obtained in large, white, rhombic prisms, which melt at 138° . The acid is soluble in the usual organic solvents, and sparingly so in hot water:

0.2148 gave 0.2101 CO_2 and 0.0599 H_2O . $\text{C}=26.6$; $\text{H}=3.1$.

0.1665 „ 0.1941 AgBr . $\text{Br}=49.9$.

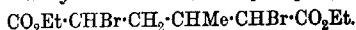
$\text{C}_7\text{H}_{10}\text{O}_4\text{Br}_2$ requires $\text{C}=26.4$; $\text{H}=3.1$; $\text{Br}=50.3$ per cent.

Methyl $\alpha\delta$ -Dibromo- β -methyladipate,



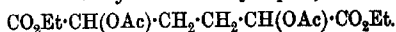
This was obtained from the bromo-acid chloride on treatment with methyl alcohol. It is a colourless liquid boiling at $167\text{--}168^\circ/12$ mm., and could not be prepared in the solid form; a yield of 64 per cent. of the acid used was obtained.

Ethyl $\alpha\delta$ -Dibromo- β -methyladipate,



This was prepared in an analogous manner to the above; it is a colourless liquid, which distils at $180^\circ/10$ mm., and also does not solidify; a yield of 72 per cent. of the acid used was obtained. Even when these esters were prepared by esterification of the solid $\alpha\delta$ -dibromo- β -methyladipic acid they could not be obtained in the solid state.

Ethyl $\alpha\delta$ -Diacetoxyadipate,



This ester was obtained by heating in an oil-bath 36 grams of ethyl $\alpha\delta$ -dibromo- β -methyladipate with twice the theoretical quantity of fused potassium acetate (40 grams) in a large excess of glacial acetic acid, at 160° for eight hours. The product was poured into water, the ester extracted several times with ether, and the ethereal solution shaken several times with dilute sodium carbonate solution to remove traces of acetic acid, washed with distilled water, and dried. On removal of the ether the ester was distilled, and a colourless liquid boiling at $195^\circ/10$ mm. was obtained; this, on cooling, gave a white solid, which crystallised from ethyl alcohol in small, white needles, melting at 73° . (Yield, 15 grams.) The pure diacetate can be distilled without decomposition under the ordinary pressure:

0.1466 gave 0.2861 CO_2 and 0.0898 H_2O . $\text{C}=53.2$; $\text{H}=6.5$.

$\text{C}_{14}\text{H}_{22}\text{O}_8$ requires $\text{C}=52.7$; $\text{H}=6.8$ per cent.

Ethyl $\alpha\delta$ -Diacetoxy- β -methyladipate,
 $\text{CO}_2\text{Et}\cdot\text{CH}(\text{OAc})\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CO}_2\text{Et}.$

This was obtained in the same way as the previous compound. It is a white solid, which crystallises from ethyl alcohol in white needles melting at 66° , and boiling at $182^\circ/10$ mm.:

0.1022 gave 0.2031 CO_2 and 0.0647 H_2O . $\text{C}=54.3$; $\text{H}=7.04$.

$\text{C}_{15}\text{H}_{24}\text{O}_8$ requires $\text{C}=54.2$; $\text{H}=7.2$ per cent.

Both diacetoxy-compounds, like the corresponding dibromo-compounds, occur in two modifications, namely, as liquids and solids.

Ethyl $\alpha\delta$ -Diphthaliminoadipate,
 $\text{CO}_2\text{Et}\cdot\text{CH}\left(\text{N}\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\right)\text{C}_6\text{H}_4\right)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\left(\text{N}\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\right)\text{C}_6\text{H}_4\right)\cdot\text{CO}_2\text{Et}.$

This ester was obtained by heating 50 grams of ethyl $\alpha\delta$ -dibromoadipate with 70 grams of potassium phthalimide, using a quarter of a molecule excess of the latter, in xylene in an oil-bath at 135 – 140° for twenty-four hours, the xylene being gradually distilled from the product during the last hour of the heating. The crude product obtained, which was a deep honey-yellow, semi-solid cake, was then poured into water and distilled in a current of steam to remove remaining traces of xylene. On cooling, the product was extracted with carbon disulphide, which separates the excess of phthalimide from the condensation product, only the latter being soluble in carbon disulphide. The extract was then dried, the carbon disulphide removed by distillation, and the oily residue submitted to distillation under diminished pressure. A pale yellow liquid boiling at 200 – $210^\circ/10$ mm. was obtained, and it solidified on cooling to a white solid, which crystallised from ethyl alcohol in colourless needles melting at 115° . It is soluble in methyl or ethyl alcohols, and very soluble in carbon disulphide:

0.1731 gave 0.3976 CO_2 and 0.0739 H_2O . $\text{C}=62.77$; $\text{H}=4.77$.

0.1701 „ 7.4 c.c. N_2 at 18° and 754 mm. $\text{N}=5.58$.

$\text{C}_{23}\text{H}_{24}\text{O}_8\text{N}_2$ requires $\text{C}=63.3$; $\text{H}=4.8$; $\text{N}=5.7$ per cent.

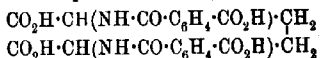
$\alpha\delta$ -Diphthaliminoadipic Acid,
 $\text{CO}_2\text{H}\cdot\text{CH}\left(\text{N}\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\right)\text{C}_6\text{H}_4\right)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\left(\text{N}\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}\right)\text{C}_6\text{H}_4\right)\cdot\text{CO}_2\text{H}.$

This acid was obtained from the above ester by (a) hydrolysis of the ester with an excess of a glacial acetic acid solution of hydrogen bromide at the ordinary temperature, or (b) by hydrolysis of the ester with the necessary quantity of alcoholic potassium hydroxide. In the first case (a), the acid was obtained directly as a solid on

addition of water to the glacial acetic acid solution. In the other case (b), the free acid was obtained from the alkaline solution on addition of hydrochloric acid in the cold. It is a pale yellow, crystalline powder, which does not melt at 270° , and is soluble in glacial acetic acid, from which it can be crystallised. It is insoluble in water, but sparingly soluble in ethyl alcohol.

0.2016 gave 0.4434 CO_2 and 0.0724 H_2O . $\text{C}=60.00$; $\text{H}=3.96$.
 $\text{C}_{22}\text{H}_{10}\text{O}_8\text{N}_2$ requires $\text{C}=60.5$; $\text{H}=3.7$ per cent.

$\alpha\delta$ -Diphthalaminoadipic Acid,



Twenty-four grams of ethyl $\alpha\delta$ -diphthaliminoadipate were treated with a solution of 20 grams of potassium hydroxide dissolved in its own weight of water; a vigorous reaction set in, and when this had subsided the mixture was heated on the steam-bath for some time until a clear solution had been obtained. The solution was then cooled on ice and carefully neutralised with the exact quantity of 5*N*-hydrochloric acid. A solid separated, which was washed free from potassium chloride with water, and crystallised from hot water. It was obtained as a fine, crystalline powder, which when dried at the ordinary temperature contains two molecules of water of crystallisation:

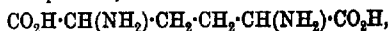
0.1960 gave 0.3804 CO_2 and 0.0736 H_2O . $\text{C}=52.3$; $\text{H}=4.7$.
 0.7510 lost 0.0532 at 100° . $\text{H}_2\text{O}=7.08$.
 $\text{C}_{22}\text{H}_{20}\text{O}_{10}\text{N}_2\cdot 2\text{H}_2\text{O}$ requires $\text{C}=52.00$; $\text{H}=4.7$; $\text{H}_2\text{O}=7.08$ per cent.

A sample of the acid dried at 100° gave the following results:

0.1252 gave 0.2570 CO_2 and 0.0516 H_2O . $\text{C}=55.3$; $\text{H}=4.3$.
 $\text{C}_{22}\text{H}_{20}\text{O}_{10}\text{N}_2$ requires $\text{C}=55.9$; $\text{H}=4.2$ per cent.

The acid after being dried at 100° is insoluble in hot water, but soluble in sodium carbonate solution, from which it is again precipitated in the insoluble form on addition of hydrochloric acid. On fusion the acid begins to decompose at 119° with evolution of carbon dioxide.

$\alpha\delta$ -Diaminoadipic acid,



was obtained by treating the above acid with concentrated hydrochloric acid, the free acid being obtained by neutralising the solution of the hydrochloride with dilute aqueous ammonia.

The crude acid was converted into the copper salt by boiling with an aqueous suspension of copper hydroxide, filtering, and

allowing the copper salt to crystallise. It is obtained in this way in blue, crystalline plates:

0.5840 gave Cu = 22.7.

0.4527 lost 0.0591 at 110°. $H_2O = 13.02$.

$C_8H_{10}O_4N_2Cu \cdot 2H_2O$ requires Cu = 23.2; $H_2O = 13.05$ per cent.

The dried copper salt is insoluble in water. These observations are in agreement with those of Sørensen and Andersen (*Zeitsch. physiol. Chem.*, 1908, 56, 266).

The Action of Trimethylamine and Triethylamine on Methyl and Ethyl $\alpha\delta$ -Dibromoadipates, and Methyl and Ethyl $\alpha\delta$ -Dibromo- β -methyladipates respectively.

Methyl $\alpha\delta$ -dibromoadipate (64 grams) was heated in sealed tubes with a slight excess over the theoretical quantity of a 33 per cent. alcoholic solution of trimethylamine for thirty-eight hours at 100–105°. The product was diluted with anhydrous ether in order to separate trimethylamine hydrobromide, filtered, and the filtrate poured into water, extracted with a further quantity of ether, and the ethereal extract washed several times with dilute hydrochloric acid. The dried ethereal extract was evaporated, and the residue submitted to distillation under diminished pressure.

A colourless liquid began to distil at 185°/12 mm., and solidified on cooling to a white, crystalline solid, which was unsaturated and free from bromine; after crystallisation from ethyl alcohol it melted at 158°, which is the melting point of methyl muconate (*Ber.*, 1902, 35, 1148). The yield was about 3 grams of solid ester, which was hydrolysed by means of methyl-alcoholic potassium hydroxide to the free acid. This was crystallised from hot water, and a white, crystalline powder melting and decomposing at 298° was obtained.

Replacing the methyl ester by the ethyl ester made no difference in the actual yield of muconic acid. The ethyl ester of muconic acid distilled at 200°/12 mm.

In a similar way ethyl and methyl $\alpha\delta$ -dibromoadipates were heated with triethylamine diluted with dry benzene in a sealed tube for the same time at 110°. The same unsaturated esters were obtained, but the yield did not improve.

The washings obtained by treating the ethereal extract with hydrochloric acid were evaporated nearly to dryness with animal charcoal, filtered, and then evaporated to dryness under diminished pressure; a white, crystalline solid was obtained, which on treatment with moist silver oxide gave the characteristic odour of trimethylamine. After removing the silver chloride formed, the filtrate was concentrated in a vacuum, and a viscid, syrupy liquid

remained, which, however, did not distil, and nothing of definite composition could be isolated.

Ethyl β -methylmuconate, $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, was obtained in a similar way to that stated above when ethyl α -di-bromo- β -methyladipate was treated with trimethylamine in 33 per cent. alcoholic solution, or with triethylamine in dry benzene. As in the previous case, the yields were very poor, and the substitution of the methyl ester caused no alteration in the result. A basic substance was apparently removed, as in the case of the adipic compound, on washing the ethereal extract with hydrochloric acid; but on similar treatment no compound of definite composition could be isolated. The ethyl ester is a colourless liquid boiling at $175^\circ/10$ mm., which showed a tendency to crystallise, but remained in a semi-solid condition.

Methyl β -methylmuconate, $\text{CO}_2\text{Me}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$, obtained by the same method as in the case of the ethyl ester described above, is a colourless liquid boiling at $145^\circ/9$ mm. It could not be obtained in the solid state.

In some experiments we have found that ethyl-alcoholic barium hydroxide also gave very good results when used to hydrolyse these unsaturated esters, especially in the case of the esters of β -methylmuconic acid. The two esters above were hydrolysed with alcoholic barium hydroxide, and the free β -methylmuconic acid was obtained by precipitating the barium salt with dilute hydrochloric acid.

β -Methylmuconic acid, $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, is a white solid which crystallises from hot water as a crystalline powder; it may also be crystallised from acetic acid, and melts and decomposes at 235° :

0.1054 gave 0.2077 CO_2 and 0.0486 H_2O . $\text{C}=53.74$; $\text{H}=5.12$.
 $\text{C}_7\text{H}_8\text{O}_4$ requires $\text{C}=53.84$; $\text{H}=5.12$ per cent.

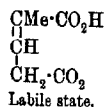
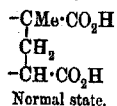
THE VICTORIA UNIVERSITY,
 MANCHESTER.

XXXIII.—The Chemistry of the Glutaconic Acids. Part VII. The Normal and Labile Forms of *α -Dimethylglutaconic Acid and their Reduction to cis- α -Dimethylglutaric Acid.*

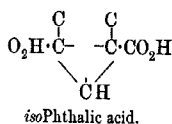
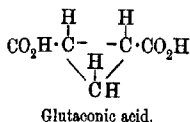
By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD.

THE experiments described in the preceding parts of this series have led to the conclusion (T., 1912, 101, 1740) that the so-called stereoisomeric forms of the "mobile" acids of this group are in reality

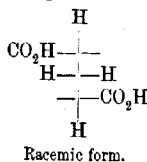
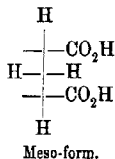
structural isomerides, which may be represented in the case of, for example, α -methylglutaconic acid, by the expressions:



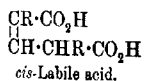
The conclusion was also drawn (*ibid.*, p. 871) that there is considerable analogy between the normal states of these acids and the corresponding 1:3-dicarboxylic acids of the aromatic series, and that the normal state of, for example, glutaconic acid, may be considered as analogous to *isophthalic acid*:



and that, therefore, this state is to be regarded as the meso- or non-resolvable form, and as having a *cis*-structure in which both carboxyl groups are on the same sides of the terminal tetrahedrons; the racemic or *trans*-modification being incapable of existence*:



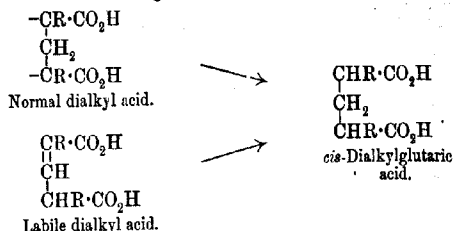
At the same time the weight of experimental evidence points to the conclusion that the labile forms of the acids of this series also possess a structure in which both carboxyl groups are on the same sides of the terminal tetrahedrons, and that it is only in special circumstances, that is to say, when groups of high molecular weight enter the molecule, that sufficient stability is conferred on this state to render the *trans*-modification capable of isolation (*ibid.*, p. 1739):



There appears to be only one way by which the *cis*-configuration of the two states of these acids can be definitely proved, and that is

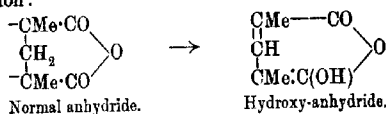
* This conclusion is also supported by the experiments carried out by Mr. C. R. Young, of this University, which show that the brucine salt of glutaconic acid cannot be separated into fractions differing in their rotatory power.

by choosing some derivative of glutaconic acid substituted by the same alkyl group on both the α - and γ -carbon atoms, and by reducing both the normal and labile states of this acid to the corresponding derivative of glutaric acid. If our assumption is correct, then both the normal and labile forms should yield the *cis*-modification of the substituted glutaric acid, thus:



The acid best suited for our purpose was evidently $\alpha\gamma$ -dimethylglutaconic acid, because the well-defined forms of $\alpha\gamma$ -dimethylglutaric acid, melting at 128° and 141° respectively, are readily recognisable; and, moreover, the presence of any *trans*-modification mixed with its *cis*-isomeride could be detected owing to the production of the equilibrium mixture of the two forms which melts at 105° .

$\alpha\gamma$ -Dimethylglutaconic acid has been described in Part II. of this series (T., 1911, 99, 2217), and was shown to yield both the normal and hydroxy-anhydride, the former being converted into the latter on distillation:



Both the normal and hydroxy-anhydride yielded the normal acid melting at 147° on treatment with water, and it was not found possible to isolate the labile modification of the acid. Since that time, however, more experience has been gained respecting the treatment necessary for the isolation of the labile acids of this series, and we now find that under suitable conditions the hydroxy-anhydride of $\alpha\gamma$ -dimethylglutaconic acid can be converted into the labile form of the acid which is a well-defined substance melting at 118° . Labile $\alpha\gamma$ -dimethylglutaconic acid, like the other labile acids of this series, is readily converted into the normal acid on treatment with mineral acids, but is remarkably stable towards alkali, and can be boiled with a concentrated aqueous solution of this reagent without undergoing change. It was therefore reduced by sodium amalgam, in aqueous solution, without carbonic acid.

The completely reduced product was found to be *cis*- α -dimethylglutaric acid melting at 128° ; no trace of the *trans*-modification or of the equilibrium mixture could be detected.

The reduction of the normal form of α -dimethylglutaconic acid was effected under similar conditions, but in the first instance it was proved by experiment that this form of the acid is not affected by concentrated alkali. It will be remembered that the normal form of β -methylglutaconic acid is completely converted into the salt of the labile acid on being boiled with a concentrated aqueous solution of potassium hydroxide, and it therefore follows that, if the normal form of α -dimethylglutaconic acid behaved in the same manner, reduction in alkaline solution might cause a partial conversion of one form into the other, and hence detract from the value of the experiment. As a matter of fact, it was found that the normal acid is quite unaltered even on prolonged boiling with concentrated aqueous alkali, and the reduction was therefore carried out under the same conditions as were employed with the labile acid; at the same time, a similar experiment was conducted in the presence of excess of carbonic acid, and in both cases the completely reduced product was found to be *cis*- α -dimethylglutaric acid melting at 128° .

During these experiments it was noticed that the normal form of the acid resists the action of the reducing agent to a greater degree than the labile modification, for whereas the latter is completely reduced after the second treatment with excess of sodium amalgam, the former requires to be treated at least four times before a product is obtained which no longer decolorises permanganate.

EXPERIMENTAL.

Labile α -Dimethylglutaconic Acid, $\text{CO}_2\text{H}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$.

After several unsuccessful attempts to prepare this substance it was ultimately obtained by treating the hydroxy-anhydride with a concentrated aqueous solution of alkali hydroxide under the following conditions. Five grams of the hydroxy-anhydride were mixed with 20 c.c. of a 50 per cent. solution of potassium hydroxide, and kept with constant shaking at a temperature of 30° . At the end of five hours the clear, colourless solution was diluted with water and mixed with rather less than the theoretical amount of hydrochloric acid required to neutralise the free alkali in the solution. The liquid was transferred to a separating funnel, covered by ether, and then treated with slightly more than the amount of hydrochloric acid required to combine with the remaining quantity of sodium salt in solution. The acid was added in small portions at a

time, and after each addition the funnel was vigorously shaken. The ether was then separated, dried, and evaporated, when it left an oily residue which solidified on being scratched, and was obtained in microscopic needles melting at 118° by crystallisation from a little water:

0.2072 gave 0.4023 CO_2 and 0.1143 H_2O . $\text{C}=52.95$; $\text{H}=6.13$.

$\text{C}_7\text{H}_{10}\text{O}_4$ requires $\text{C}=53.2$; $\text{H}=6.3$ per cent.

The mother liquor from the ether extraction yielded on further extraction an acid which evidently contained a small amount of the normal acid.

The labile acid is more soluble in water and in ether than its normal isomeride, but does not differ from it in its behaviour towards metallic salts. There is a marked difference in the behaviour of the two compounds towards acetyl chloride, for when the labile acid is treated with this reagent under the same experimental conditions that produce the normal anhydride from the normal acid (T., 1911, 99, 2235), it is converted into the hydroxy-anhydride melting at 75° .

The Reduction of the Labile Acid to cis- α -Dimethylglutaric Acid.

The reduction was effected by sodium amalgam in aqueous solution. Ten grams of the acid dissolved in dilute alkali were treated with successive portions of 29 grams of sodium as 3 per cent. amalgam, the solution being cooled throughout the reduction by running water. Since the acid extracted from the acidified product by ether still possessed the property of decolorising alkaline permanganate, the reduction was repeated with the same amount of amalgam as before. The final product, which was solid, did not reduce permanganate; it was crystallised from water, and obtained in needles melting at 128° . (Found, $\text{C}=52.41$; $\text{H}=7.53$. $\text{C}_7\text{H}_{12}\text{O}_4$ requires $\text{C}=52.5$; $\text{H}=7.5$ per cent.)

The acid was characterised as *cis- α -dimethylglutaric acid* by conversion into the anhydride melting at 95° by the action of acetyl chloride. Excepting for a trace of a solid of lower melting point, this acid appeared to be the only substance formed by the reduction of the labile acid.

The Reduction of the Normal Acid to cis- α -Dimethylglutaric Acid.

In the first instance it was proved by experiment that the normal acid is not affected by prolonged boiling with 20 per cent. aqueous alkali, and for this purpose the acid dissolved in the alkali was heated to the boiling point for five hours. The acid was extracted

practically unchanged, from the acidified solution, by ether. The reduction was then carried out in precisely the same manner as with the labile acid, only in this case the product did not cease to decolorise permanganate until the reduction had been effected four times. The recrystallised acid melted at 128° (Found, $C=52.38$; $H=7.58$. $C_7H_{12}O_4$ requires $C=52.5$; $H=7.5$ per cent.), and gave the characteristic anhydride of *cis- α -dimethylglutaric acid* on treatment with acetyl chloride. In this case also no trace of the *trans*-acid could be detected, although, as was to be expected from the repeated extractions with ether, the yield of the saturated acid was considerably less than in the case of the labile acid.

In order to show that the alkali hydroxide generated during the reduction had no effect on the nature of the product, a similar reduction was carried out in the presence of excess of carbonic acid. The same result was obtained.

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XXXIV.—*The Measurement of Tryptic Protein Hydrolysis by Determination of the Tyrosine Liberated.*

By SAMUEL JAMES MANSON AULD and THOMAS DUNCAN
MOSSCROP, B.Sc.

Of the numerous methods described for following the course of protein hydrolysis, that described by Brown and Millar (T., 1906, 89, 145) apparently offers many advantages, since it is volumetric in character, easy of manipulation, and in the hands of these authors gave good results. The method, in brief, is based on the estimation, by absorption of bromine, of the tyrosine formed during tryptic digestion, and is carried out along the lines suggested by J. H. Millar (*Trans. Guinness Research Laboratory*, 1903, Part I.). The tyrosine-containing liquid is acidified with hydrochloric acid to which sodium bromide is added, and the solution thus obtained is titrated with standard sodium bromate solution. The product of reaction is dibromotyrosine.

We had occasion to study this method during the preliminary work attending another investigation, and found that, as originally described, the method is difficultly workable, but can be made useful by the introduction of several modifications.

Use of Starch and Potassium Iodide as Indicator.

J. H. Millar originally used the persistence of the yellow colour of bromine to mark the end-point of the reaction, but also states that starch and potassium iodide may be used as indicator of free bromine. The latter method was adopted by Brown and Millar.

In colourless solutions the yellow colour induced by excess of bromine may certainly be used to show the completion of the reaction, but this is impossible in ordinary protein digests, and the use of starch and iodine is also impossible, as a little consideration might show, since hydrochloric acid itself will liberate sufficient iodine from potassium iodide to cause coloration of the starch. We tried the effect of acidifying the solution with other weaker acids (such as phosphoric, citric, and acetic acids), but on keeping for a period equivalent to the length of time occupied by a titration they also liberate iodine and mask the end-point.

Use of Methyl-violet as Indicator.

Attempts were made to utilise the oxidising power of bromine in discharging the colour of organic dyestuffs, but with only partial success. Good results were, however, obtained by using the well-known stain, Gentian-violet, which shows marked colour changes. Gentian-violet is the commercial name given to a mixture of Methyl-violet, Crystal-violet, and dextrin, and the colour changes were found to be due to the Methyl-violet (pentamethylpararosaniline hydrochloride). In the acid solution used for titration this dyestuff becomes olive-green, and the addition of sodium bromate or traces of free bromine causes a sharp change to a deep bluish-violet. The change is very marked and exceedingly sharp, although the colour fades after several minutes. Excess of bromine or sodium bromate solution discharges the blue colour, changing it to a dirty yellow.

Rate of Bromination of Tyrosine.

Tyrosine rapidly takes up bromine to form dibromotyrosine, and the absorption at first is very rapid, but falls off considerably, under the conditions of titration, towards the end of the reaction, as is shown by the following case.

Twenty-five c.c. of *N*/25-tyrosine solution in 5 per cent. hydrochloric acid and 20 c.c. of 20 per cent. sodium bromide solution were titrated with *N*/20-sodium bromate; 0.5 c.c. of the latter was added at a time as long as the bromine was absorbed at once, and then two drops at a time until the reaction was complete.

	<i>N</i> /20-Sodium bromate used. C.c.	Tyrosine brominated. Per cent.	Time taken for absorption of bromine. sec. (normal shaking)
Up to	7.0	55.1	3.0
	8.0	62.9	3.5
	9.0	70.8	6.0
	11.0	86.6	9.0
	12.0	94.5	25.0
	12.4	97.6	2 min.
	12.6	99.2	permanent after 30 min.

The falling off of the rate of bromination shows the impossibility, in any case, of the use of starch and potassium iodide as indicator, and precludes the use of any indicator within the experimental liquid, since free bromine may be present for a short time in the solution, and yet be absorbed by the tyrosine on keeping.

Method Used.

Indicator.—Methyl-violet or Gentian-violet may, however, be satisfactorily used as an outside indicator. The colouring matter is made of 1 per cent. strength in 70 per cent. alcohol, and about ten drops of the solution are added to 10 c.c. of 5 per cent. hydrochloric acid. This liquid is dotted over a white tile in the usual manner, and tested with the experimental liquid from time to time. With a little practice and after doing a preliminary titration the end of the reaction, as indicated by the formation of the blue colour, may be detected with accuracy.

On the tile, water alone produces a very similar colour, but dilute acid effects no change. Free bromine water of all strengths will not give the colour change, but does so with practically the same delicacy when dissolved in sodium bromide solution. This may be due to the formation of an unstable perbromide or similar compound with the Methyl-violet, or possibly to its action as nascent bromine (as in the actual titration of acid bromide solution with sodium bromate), the sodium bromide solution acting as $\text{NaBr}, x\text{Br}$.

Procedure.—The solution to be titrated is made of not more than 5 per cent. acidity with hydrochloric acid. A lower concentration of acid than 2 per cent. turns the indicator blue, whilst a higher concentration than 5 per cent. turns it yellow. To the acid solution is added 15–20 c.c. of 20 per cent. sodium bromide, and the liquid is then titrated with *N*/20-sodium bromate. Brown and Millar used *N*/5-sodium bromate solution for titration, but since it is seldom that more than 1 c.c. of solution of such strength is required, more accurate results are obtained by using the more dilute liquid.

Towards the end of the reaction at least thirty seconds should

elapse between successive additions of the sodium bromate, and the reaction is best carried out in a stoppered bottle, which can be vigorously shaken after each addition.

Under these conditions sufficiently accurate, comparable results can be obtained to make the method extremely useful. Dibromotyrosine only is apparently formed. Sodium bromate corresponding with 6 molecules of bromine were added to a known weight of tyrosine dissolved in dilute hydrochloric acid, and mixed with sodium bromide, and the mixture allowed to remain for twenty-four hours. At the end of that time the excess of bromine was estimated, and the amount absorbed was found to be practically only 2 molecules.

The following results were obtained with tyrosine and tyrosine-containing mixtures of strengths unknown at the time:

Weight of tyrosine used. Gram.	N/20-Bromate solution used. C.c.	Weight of tyrosine found. Gram.	Error. Per cent.
0.1274	9.80	0.1274	nil.
0.1460	11.45	0.1495	+2.3
0.1559	11.80	0.1576	1.09
*0.1000	7.60	0.1010	1.0
*0.0481	3.65	0.0483	0.4

* In solutions containing tyrosine, leucine, asparagine, and ammonium chloride.

Experiments carried out with edestin digested in dilute sodium carbonate solution with trypsin, and corrected for the bromine absorbed by the protein, confirmed Brown and Millar's contention that the method can be used for determining tyrosine in presence of proteins and other early cleavage products, and also that practically the whole of the tyrosine is liberated in the first stages of tryptic digestion.

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XXXV.—*The Solubility of Sulphanilic Acid and its Hydrates.*

By JAMES CHARLES PHILIP.

IN the course of another research it became desirable to ascertain exactly the conditions of stability of the different hydrates of sulphanilic acid. According to earlier investigations (see Laar, *J. pr. Chem.*, 1879, 20, 242; *Ber.*, 1881, 14, 933), both dihydrate

and monohydrate exist, but the conditions of temperature and concentration under which they separate from solution have not been determined. The solubility of sulphanilic acid has accordingly been measured at a number of temperatures between 0° and 55° , whilst, in addition, the composition of the solid phase in equilibrium with the saturated solution was determined in each case.

The investigation has shown that the stable solid in contact with the saturated solutions is dihydrate from 0° to 21° , monohydrate from 21° to 40° , and anhydrous acid from 40° upwards. In previous determinations of the solubility of sulphanilic acid (see Dolinski, *Ber.*, 1905, **38**, 1835), this change in the character of the solid phase as the temperature rises has been overlooked, and the attempt has been made to represent the variation of solubility with temperature as a continuous curve. As will be seen from the determinations of solubility recorded below, this cannot be done. In some cases, indeed, two distinct values were obtained for the solubility at a given temperature, and investigation revealed the fact that the difference in solubility was associated with a difference in the solid phase present.

The equilibrium between the solid hydrates and the water vapour in the surrounding atmosphere also presents points of interest. Chief among these is the difference in the behaviour of the dihydrate and the monohydrate in regard to dehydration. Under conditions in which the monohydrate is unaltered, the dihydrate loses all its water, and leaves the anhydrous acid. This is probably due to suspended transformation in the case of the monohydrate, but it has been frequently observed that the rate of dehydration of the dihydrate exhibits no change at the point corresponding with the monohydrate. This fact suggests that the molecules of the dihydrate, when deprived of water, may yield those of the anhydrous acid directly, without passing through the monohydrate stage, and further evidence of this kind, if obtainable, would throw light on the manner in which the water molecules are attached in compounds containing water of crystallisation.

Whilst this appears to be the normal course of dehydration of the dihydrate, it was observed in a few cases that the process stopped at the monohydrate stage, although the conditions were those in which other samples of the dihydrate had lost all their water.

From experiments in which the hydrates were kept in closed vessels over sulphuric acid of different strengths, and weighed from time to time, the dissociation pressures were deduced. At 20° the dihydrate remains of constant weight in an atmosphere with an aqueous vapour pressure higher than about 16.5 mm. of mercury,

whilst the corresponding limit for the monohydrate is about 12 mm. of mercury. The latter figure was confirmed by direct measurement of the dissociation pressure in a tensimeter.

EXPERIMENTAL.

The sulphanilic acid employed in the investigation was obtained by recrystallisation of the best commercial acid. The purity of the recrystallised material was established by dissolving a known quantity in water, and titrating with a carefully standardised sodium hydroxide solution.

In the determination of solubility the point of equilibrium was reached from both sides. In one tube, water was stirred up with excess of sulphanilic acid; in another tube, a solution which had been saturated at a somewhat higher temperature was treated similarly. The two tubes were immersed in a constant temperature bath, and the stirring was continued for six to seven hours at least. The equality of the values obtained for the solubility in the parallel experiments was a guarantee that equilibrium between solid and solution had really been reached. In some cases, where intermittent shaking was employed instead of continuous stirring, the time of contact of solid with solution was correspondingly longer.

When sufficient time had been allowed for the attainment of equilibrium, two samples of the saturated solution were drawn into separate pipettes through cotton-wool plugs, and immediately discharged into weighed flasks. In this way, known weights of saturated solution were obtained, and the sulphanilic acid present was then estimated by titration with standard sodium hydroxide solution.

When the extracts had been made, the remaining solution, along with the excess of solid, was thrown on a filter, and the liquid was removed as completely as possible with the aid of a pump. After the solid had been further dried by pressing between filter paper for about ten minutes, a portion was weighed out and left overnight in a vacuum desiccator containing concentrated sulphuric acid. In these circumstances the water of crystallisation of sulphanilic acid is rapidly and completely removed. The dihydrate contains 17.2 per cent. of water, and the monohydrate 9.42 per cent., so that this method of examination showed clearly whether the solid in equilibrium with the saturated solution had been dihydrate, monohydrate, or anhydrous acid.

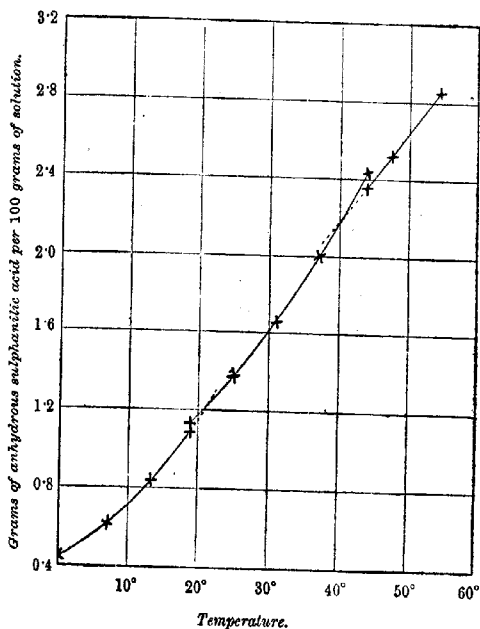
The results obtained for the solubility are recorded in the following table, and are represented graphically in Fig. 1. The temperatures shown in the table are corrected values, based on

a comparison of the thermometers actually used with a standard instrument.

Grams of anhydrous acid per 100 grams		Solid phase.	Grams of anhydrous acid per 100 grams		Solid phase.
Temp.	of solution.		Temp.	of solution.	
0.0°	0.444	dihydrate	31.1	1.662	monohydrate
7.2	0.822	"	37.2	2.004	"
13.3	0.841	"	44.0	2.44	"
18.9	1.093	"	44.0	2.36	anhydrous acid
18.9	1.187	monohydrate	47.5	2.52	"
25.1	1.384	"	54.5	2.85	"

Particular interest attaches to the figures obtained at 18.9° and 44.0°. In two experiments at the former temperature, different

FIG. 1.



values of the solubility were recorded, and examination of the solid phase in each case showed that the higher value was obtained in presence of the monohydrate, which is metastable at 18.9°, whilst the lower solubility was given by the stable dihydrate. Similarly, at 44.0°, the higher value of the solubility was given by the mono-

hydrate, which is the metastable phase at this temperature also, and the lower value by the anhydrous acid.

The dihydrate of sulphanilic acid, obtained by crystallisation from its solutions below 20° , is a highly efflorescent substance, and, if exposed to the air of the room, loses almost all its water in twelve hours, ultimately becoming anhydrous. The monohydrate, on the other hand, has on several occasions been similarly exposed, side by side with the watch-glass containing the dihydrate, without losing weight at all. In one experiment, indeed, the monohydrate retained its weight unchanged for over a fortnight, and even then showed no sign of losing water. This may be an instance of suspended transformation, but the comparative rates of dehydration of the two hydrates, obtained in other experiments, indicate that the process is different in the two cases.

A specimen of the monohydrate, kept in a closed vessel (a desiccator) over 49 per cent. sulphuric acid, lost weight slowly, and after two days still retained half its water of crystallisation. A specimen of the dihydrate, on the other hand, exposed in the same vessel, lost weight rapidly, as shown by the following record:

Time of exposure.	Per cent. loss of weight.
3.5 hours	6.7
7.0 "	13.3
22.5 "	17.0
After 3 hours further in a vacuum desiccator }	17.4

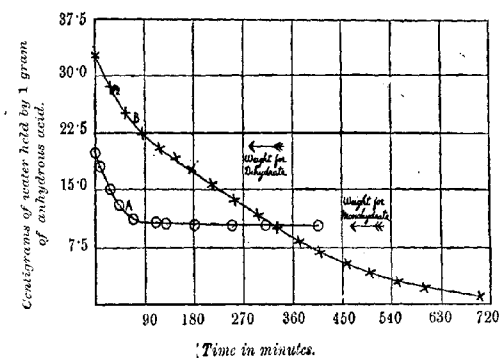
It will be seen that the dihydrate loses weight at a nearly uniform rate, whether its content of water is above or below that corresponding with the monohydrate. It is true that the rate of loss of weight becomes lower when dehydration is nearly complete, but the uniform rate persists until the point corresponding with the monohydrate is well passed.

The difference in the behaviour of monohydrate and dihydrate is clearly brought out by Fig. 2, in which two dehydration curves, similar to many others which have been recorded, are reproduced. Slightly moist crystals of the monohydrate were weighed out on a watch-glass, and this was kept all the time in the balance case, the air in which was partly dried by a few dishes containing concentrated sulphuric acid. Weighings made from time to time showed how the dehydration was proceeding. The curve *A*, obtained by plotting the weight of water (in centigrams) held by 1 gram of anhydrous acid at various times, shows that in the case of the monohydrate the mechanically held moisture comes off rapidly, and that when the composition has reached the point corresponding with a water content of 1 molecule per molecule of anhydrous acid, there

is practically no further loss of weight under the conditions of the experiment. Curve *B* is a graphical reproduction of the corresponding record obtained with slightly moist crystals of dihydrate exposed to the same conditions. The chief features of curve *B* are the change of slope about the point corresponding with the dihydrate, and the absence of a break, or even a change of direction, at the point corresponding with the monohydrate. It is perhaps worth noting that the crystals, whether of monohydrate or dihydrate, employed in these experiments, had been filtered from their mother liquors and then transferred directly to the watch-glasses without grinding or further drying.

It has been suggested above that the absence of change in the monohydrate under certain conditions is probably due to suspended

FIG. 2.



transformation. In connexion with this, a comparative experiment was made with two specimens of monohydrate derived from the same crystallisation, one of which, however, was finely ground, whilst the other was not so treated. On exposure to the air of the room, the untreated acid remained of constant weight, whilst the finely ground specimen lost weight slowly, much more slowly than unground dihydrate under similar conditions. Although, therefore, the state of division has undoubtedly some influence on the progress of dehydration, this factor cannot adequately account for the very different rates of dehydration observed for the two hydrates.

With the object of ascertaining the dissociation pressures of the two hydrates, specimens of each were exposed in closed vessels (desiccators) containing sulphuric acid of various strengths. It was found that the monohydrate lost weight slowly over 35.4 per cent.

acid (aqueous vapour pressure about 11.6 mm. at 20°); but retained its weight unaltered over 30.9 per cent. acid (aqueous vapour pressure about 12.9 mm. at 20°). The dihydrate lost weight slowly over 14.9 per cent. acid (aqueous vapour pressure about 16.5 mm. at 20°), but showed no loss over 9.4 per cent. acid (aqueous vapour pressure about 16.9 mm. at 20°).

The author desires to express his thanks to Mr. H. R. Courtman and Mr. E. Jobling, who assisted in the preliminary stages of this investigation.

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XXXVI.—*The Alkaloids of Xanthoxylum brachyacanthum.*

By HOOPER ALBERT DICKINSON JOWETT and FRANK LEE PYMAN.

The genus *Xanthoxylum* (or *Zanthoxylum*) of the natural order Rutaceæ contains some eighty species, distributed chiefly over Africa, America, and Australia. Perhaps the best known is the Prickly Ash of North America (*X. americanum*), which is an official drug of the United States Pharmacopœia. In spite of the large number of species available, few chemical examinations of these trees have been carried out, but those results which were obtained before 1889 are dealt with in detail in the introduction to Giacosa and Soave's paper (*Gazzetta*, 1889, 19, 303) on *X. senegalense*, and there have been few since then.

For our purpose it will be sufficient to mention that although the presence of alkaloids in several species of *Xanthoxylum* has been recorded, and in particular the presence of berberine has been suspected, in no case has an alkaloidal constituent been characterised definitely, much less identified. Only in two cases have the alkaloids of a *Xanthoxylum* received more than superficial attention.

The alkaloids of *X. senegalense* (artar root) have been investigated by Giacosa and Soave (*loc. cit.*). These authors isolated two alkaloids, the principal of which they called artarine; it formed a rose-grey, amorphous mass, yielding yellow, crystalline salts, which gave on analysis figures equally in agreement for deriv-

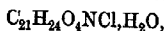
atives of the two formulae, $C_{21}H_{23}O_4N$ and $C_{20}H_{17}O_4N$; the second base, which was not analysed, formed blood-red needles and gave yellow salts.

Two alkaloids, α - and β -xantherine, have recently been isolated from *X. ochroxyllum* by Leprince (*Bull. Sci. Pharmacol.*, 1911, 18, 337). The first has the formula $C_{24}H_{23}O_6N$, but no formula is given for the second; both yield yellow salts. The properties of all these alkaloids are entirely different from those of the alkaloids of *X. brachyacanthum* now described.

The material used for the present investigation was kindly supplied to us by the authorities of the Imperial Institute, and represented the bark of *X. brachyacanthum* obtained from Queensland, Australia. A specimen was submitted to the authorities at Kew, who reported that it had the same type of structure as the bark of specimens of *Xanthoxylum brachyacanthum*, F. Muell, in the museum at Kew, and that it probably belonged to this species or some other species of *Xanthoxylum*.

Xanthoxylum brachyacanthum has not previously been the subject of a chemical examination. The physiological properties of a tincture of the bark were, however, described to the Therapeutic Society by Dr. J. Gordon Sharp in 1906; these properties are not in accord with those observed by our collaborator, Dr. P. P. Laidlaw, for the pure alkaloids which we have isolated.

Preliminary examination showed that the bark contained a large amount of alkaloid which was readily extracted by dilute acids. When the extract was rendered alkaline with sodium carbonate or sodium hydroxide, however, only a very small amount of alkaloid was removed by extraction with chloroform, and it was, therefore, found necessary to employ a special method, which is described in the experimental part of this paper. It was then found that an alkaloid which was obtained in the form of its chloride,



was present in large amount (1.85 per cent.), together with a small quantity (0.06 per cent.) of a second base having the composition $C_{21}H_{23}O_4N, \frac{1}{2}EtOH$.

The chloride of the alkaloid present in large amount melted at 262° (corr.), and the corresponding iodide, $C_{21}H_{23}O_4NI$, melted at 220° (corr.). This alkaloid contained two methoxyl groups, and one *N*-methyl group; it also contained a methylenedioxy-group, since it gave a positive result when Gaebel's test (*Arch. Pharm.*, 1910, 248, 226) was applied. The chloride after drying had $[\alpha]_D - 137.0^\circ$.

The chloride was not decomposed by sodium hydroxide, and after treatment with silver hydroxide gave a very strongly alkaline

aqueous solution, which on evaporation deposited an unsaturated anhydro-base, $C_{21}H_{23}O_4N$, which melted at $111-112^\circ$ (corr.).

This chief alkaloidal constituent of the bark was thus shown to be a quaternary base, and its composition and properties suggested that it might be one of the two possible varieties of *l*-canadine (*l*-tetrahydroberberine) methochloride.

The methochlorides of *l*-canadine have not previously been described, but E. Schmidt (*Arch. Pharm.*, 1894, **232**, 136) has given the melting point of *l*-canadine methiodide as $228-232^\circ$. The recent work of Voss and Gadamer (*Arch. Pharm.*, 1910, **248**, 43), however, rendered it probable that Schmidt's methiodide was a mixture, for these authors have shown that *l*-canadine combines with ethyl iodide to form a mixture of the α - and β -ethiodides, the isomerism of which is due to the asymmetry of the nitrogen atom. They separated the two salts by crystallisation, then preparing from them the corresponding methochlorides, and characterised the salts with the following results:

l-Canadine Ethyl Salts (Voss and Gadamer).

	M. p.	$[\alpha]_D$.
α -Ethochloride, $C_{22}H_{26}O_4NCl \cdot 2H_2O$	233°	-127.3°
β -Ethochloride, $C_{22}H_{26}O_4NCl \cdot 2H_2O$	245	-138.3
α -Ethiodide, $C_{22}H_{26}O_4NI \cdot 1\frac{1}{2}H_2O$	187	-91.5
β -Ethiodide, $C_{22}H_{26}O_4NI$	225	-115.3

They further showed that the α -variety could be converted into the β -form by the action of heat, as in the case of certain dialkylconium iodides containing both an asymmetric carbon atom and an asymmetric nitrogen atom which had been studied by Scholz (*Ber.*, 1905, **38**, 595). Similarly, McDavid, Perkin, and Robinson (*T.*, 1912, **101**, 1218) obtained two isomeric tetrahydroberberine benzyl chlorides by the action of benzyl chloride on tetrahydroberberine. With the object, therefore, of identifying the alkaloid from *Xanthoxylum brachyacanthum*, we have investigated the action of methyl iodide on *l*-canadine. The methiodide produced crystallised in two forms, which appeared to separate simultaneously when either water or alcohol was employed as the solvent. The mixture was, therefore, converted into the methochlorides, which fortunately proved to have an entirely diverse solubility in water, and the sparingly soluble form—the β -variety—was readily obtained in a pure state by recrystallisation from this solvent. The mother liquor when evaporated to dryness and crystallised from absolute alcohol then deposited the α -methochloride, which was purified by recrystallisation from absolute alcohol. The corresponding α - and β -methiodides were then prepared from the pure methochlorides by double decomposition with potassium iodide, and recrystallisation

from water. The properties of the salts were then found to be as follows:

l-Canadine Methyl Salts.

	M. p.	$[\alpha]_D^{25}$.
α -Methochloride, $C_{27}H_{50}O_4NCl \cdot H_2O$	262° (corr.)	-136.4°
β -Methochloride, $C_{27}H_{50}O_4NCl \cdot 6H_2O$	262	-160.9
α -Methiodide, $C_{27}H_{50}O_4NI$	220	—
β -Methiodide, $C_{27}H_{50}O_4NI$	264	—

* Of the anhydrous salts.

The methiodide of lower melting point passed into the variety of higher melting point when heated above its melting point, and is, therefore, termed the α -variety in accordance with the usage of Scholtz (*loc. cit.*).

The properties of the α -methyl salts of *l*-canadine agree with those of the quaternary alkaloid from *Xanthoxylum brachyacanthum*, and mixed melting-point determinations of the methochloride and methiodide confirmed the identity of the salts from either source. The quaternary chloride isolated from *Xanthoxylum brachyacanthum* is, therefore, *l*- α -canadine methochloride.

This is the first record, so far as we are aware, of the isolation from a plant of a substance containing an asymmetric nitrogen atom.

The physiological examination of the α - and β -methochlorides of *l*-canadine gave an interesting result. It is, of course, well known that the stereochemical configuration of substances containing an asymmetric carbon atom often profoundly effects their physiological action, as, for examples, hyoscyamine, adrenaline, and pilocarpine. Very little is known, however, of the relative physiological behaviour of compounds the stereoisomerism of which is due to the asymmetry of a nitrogen atom. The only instance hitherto recorded in the literature is that of the dialkylconium iodides. Scholtz (*loc. cit.*) states on the authority of Hildebrandt that here the α -salts were less toxic than the β -salts; thus the doses of α - and β -ethylbenzylconium iodides which were just sufficient to cause paralytic curare-like action in medium-sized frogs were 2.6 and 1.5 milligrams respectively; in the cases of propylbenzyl- and butylbenzylconium iodides, smaller differences were observed. We were consequently interested to know whether differences in the physiological action of the α - and β -methochlorides of *l*-canadine were also to be observed. Dr. P. P. Laidlaw, of the Wellcome Physiological Research Laboratories, kindly examined these salts, and found a very considerable quantitative difference in their physiological action.

On the frog neither substance caused local or general anaesthesia,

but a gradual paralysis of all voluntary muscle developed, similar to that produced by curare and ammonium bases generally. *l*- β -Canadine methochloride was found to be much more active than the α -form in this respect. On the intact frog 1 milligram of the β -compound produced complete paralysis of all voluntary muscle in twelve minutes; 0.25 milligram failed to produce complete paralysis, but the frog was profoundly affected; 2.5 milligrams of the α -salt produced severe symptoms without producing complete paralysis.

The two salts were then compared by perfusing the hind limbs of frogs with dilutions of various strengths, and determining the rate at which paralysis of the nerve endings was produced.

In this set of experiments 1/10,000 and 1/20,000 of the α -salt were found to be almost exactly equal to 1/100,000 and 1/200,000 of the β -salt respectively. It is clear, then, that in their power of producing typical curare effect the β -salt is ten times as powerful as the α -one. As, however, in the above experiments the air-dried salts were employed, the 10:1 proportion does not really represent the relationship of the molecular activities correctly. Allowing for the fact that the α -salt crystallises with one molecule of water of crystallisation, and the β -salt with six molecules, a ratio of 12 to 1 is obtained.

On the mammal again these two alkaloids have actions very similar to those of curare. They cause large falls of blood pressure, and paralyse the ganglion cells of the vagus nerve. They produce paralysis of the respiratory centre in toxic doses. Both have a mild stimulating effect on the isolated uterus of a guinea-pig. In these various actions *l*- β -canadine methochloride is very obviously more active than the corresponding α -compound, but the ratio of activity between the two forms was only determined for their paralytic effect on frog muscle.

The second alkaloid of *Xanthoxylum brachyacanthum*, the base $C_{21}H_{23}O_5N, \frac{1}{2}EtOH$, which occurred only in small amount, melted at 170–171° (corr.) after drying at 100°. It was optically inactive, contained two methoxy-groups, one *N*-methyl group, and a methylenedioxy-group. Its hydrochloride and aurichloride were also obtained in crystalline form. Its chemical and physiological properties agree closely with those given for γ -homochelidonine, and there can be no doubt as to its identity with this alkaloid.

β - and γ -Homochelidonine, which are different but interconvertible forms of the same alkaloid, have already been isolated from *Chelidonium majus*, *Sanguinaria canadensis*, and *Eschscholtzia californica* by E. Schmidt and his collaborators, and from *Buconia cordata* by Müller and Schlotterbeck and by Hopfgarten. The main

features of the physiological action of this alkaloid are described by E. Schmidt (*Arch. Pharm.*, 1893, **231**, 143) on the authority of H. Meyer.

EXPERIMENTAL.

Isolation of the Alkaloids of Xanthoxylum brachyacanthum.

The crushed bark (8.7 kilograms) was percolated with 0.25 per cent. aqueous tartaric acid until no more alkaloid was removed. The percolate was then somewhat concentrated, filtered, and precipitated with aqueous mercuric chloride solution. The precipitated mercuric chlorides were then collected, washed with water, and decomposed by hydrogen sulphide in aqueous suspension. After filtering from mercuric sulphide the liquor was evaporated to low bulk, made alkaline with sodium hydroxide, and extracted many times with chloroform (mother liquor=M.1).

The chloroform extract was evaporated to dryness and extracted with very dilute hydrochloric acid; the acid extract after filtering was rendered alkaline with sodium carbonate, and completely extracted with ether, which on distillation left about 7 grams of crude γ -homochelidonine (p. 299) as a viscous oil, which soon crystallised.

The aqueous mother liquor was then mixed with sodium hydroxide and extracted with chloroform (mother liquor=M.2). The residue left on evaporation of the chloroform was mixed with acetone, and gave 93 grams of crude *l*- α -canadine methochloride as a buff-coloured, crystalline powder, melting at 250°.

This yield amounts to 1.07 per cent. of the bark, but does not represent the whole amount of this alkaloid present, since the mother liquors M.1 and M.2 still contained further quantities, which were not, however, isolated in this experiment. In a separate, small, completed extraction with 500 grams of bark, 9.25 grams of crude, crystalline *l*- α -canadine methochloride were isolated, that is, 1.85 per cent. of the bark.

l- α -Canadine Methochloride from Xanthoxylum brachyacanthum.

The crude product isolated as previously described was crystallised, first from strong and then several times from absolute alcohol, when it was obtained in colourless, prismatic needles, which melted and decomposed at 262° (corr.). The mother liquors from this salt were evaporated to remove alcohol, dissolved in water, and precipitated as iodide by the addition of potassium iodide. After crystallisation from water, using animal charcoal, most of the remaining quantity of the alkaloid was recovered as *l*- α -canadine methiodide melting at 220° (corr.).

l-*Canadine methochloride* prepared as above crystallises with $1\text{H}_2\text{O}$. It is very readily soluble in water or hot alcohol, and easily so in cold alcohol, but insoluble in acetone:

0.1902 * gave 0.4341 CO_2 and 0.1094 H_2O . $\text{C}=62.2$; $\text{H}=6.4$.

0.6285 * lost 0.0257 at 100° . $\text{H}_2\text{O}=4.1$.

$\text{C}_{21}\text{H}_{24}\text{O}_4\text{NCl}\cdot\text{H}_2\text{O}$ requires $\text{C}=61.8$; $\text{H}=6.4$; $\text{H}_2\text{O}=4.4$ per cent.

0.0932 † gave 0.2199 CO_2 and 0.0545 H_2O . $\text{C}=64.3$; $\text{H}=6.5$.

0.1494 † „ 0.0530 AgCl . $\text{Cl}=8.8$.

$\text{C}_{21}\text{H}_{24}\text{O}_4\text{NCl}$ requires $\text{C}=64.7$; $\text{H}=6.2$; $\text{Cl}=9.1$ per cent.

A determination of the specific rotatory power of the anhydrous salt in aqueous solution gave the following result:

$\alpha_D - 11.50^\circ$; $c=4.197$; $l=2$; $[\alpha]_D - 137.0^\circ$.

l-*Canadine methiodide* crystallises from water in prisms which melt at 220° (corr.) when fairly rapidly heated. When kept at this temperature for a few seconds the molten mass begins to crystallise, and then does not melt and decompose until about 250° (corr.).

l-*Canadine methiodide* is very sparingly soluble in cold, and sparingly so in boiling water. It is anhydrous:

0.1708 gave 0.3282 CO_2 and 0.0746 H_2O . $\text{C}=52.4$; $\text{H}=4.9$.

0.3744 † „ 0.3686 AgI at $180-200^\circ$. $\text{OMe}=13.0$:

and 0.1692 AgI at $300-330^\circ$. $\text{NMe}=5.6$.

$\text{C}_{21}\text{H}_{24}\text{O}_4\text{NI}$ requires $\text{C}=52.4$; $\text{H}=5.0$; $(\text{OMe})_2=12.7$;
 $\text{NMe}=6.0$ per cent.

Methylation of l-Canadine. Formation of the α - and β -Methochlorides.

l-*Canadine* readily combines with methyl iodide when gently warmed on the water-bath, but the resulting mixture of the methiodides could not be readily separated by fractional crystallisation either from water or alcohol. It was found, however, that the solubilities of the methochlorides in water were somewhat widely apart, and the two isomerides were obtained in a pure state by means of the following process.

Thirty grams of natural *l*-*canadine*, which melted at $133-134^\circ$ (corr.) and had $[\alpha]_D - 299^\circ$ ($c=1.3264$), were boiled under a reflux condenser for half an hour with 45 c.c. of methyl iodide and 30 c.c. of methyl alcohol. The solvents were then distilled off, and the resulting mixture of *l*- α - and *l*- β -*canadine methiodides* dissolved in 1.5 litres of boiling water. This solution was digested with an excess of silver chloride, filtered from the silver salts, and the resulting solution of *l*- α - and *l*- β -*canadine methochlorides* evaporated

* Air dried.

† Dried at 100° .

‡ By Zeisel's and Herzog and Meyer's methods.

to a thin syrup and set aside to crystallise. The somewhat sparingly soluble *l*- β -canadine methochloride then separated in large, hard prisms, which were purified by recrystallisation from water. The mother liquor on concentration gave a further small quantity, and 21.2 grams of the pure salt were thus obtained; this yield represents 48 per cent. of the theoretical.

The syrupy mother liquor from which *l*- β -canadine methochloride had been thus removed was evaporated to dryness in a vacuum, and dissolved in about 10 c.c. of absolute alcohol, when on keeping, a small quantity of *l*- α -canadine methochloride separated. The mother liquors from this were again evaporated to dryness and dissolved in absolute alcohol, when a further quantity of the same salt was obtained. The two crops were then combined and recrystallised from absolute alcohol, when 4.5 grams of pure *l*- α -canadine methochloride were obtained. This salt melted at 260° (corr.) alone and when mixed with the salt derived from *Xanthoxylum brachyacanthum*; it had $[\alpha]_D -136.4^\circ$ ($c=3.7264$). A specimen of the α -methiodide prepared from it by precipitation with potassium iodide and recrystallisation from water, melted at 220° (corr.) alone or when mixed with *l*- α -canadine methiodide from *Xanthoxylum brachyacanthum*, and like the latter salt solidified just above its melting point and did not then decompose until about 250° (corr.).

The yield of *l*- α -canadine methochloride thus isolated, 4.5 grams, represents only 12 per cent. of the theoretical. There then remained a syrup which after the complete removal of the alcohol and slight dilution with water deposited a further small quantity of the β -methochloride. The syrup obviously represented a mixture of the α - and β -salts, and was not worked up further.

l- β -Canadine methochloride crystallises from water in large, colourless, oblong prisms containing $6H_2O$, of which 5 are lost at 100°. The air-dried salt partly melts in its water of crystallisation below 100°, starting to sinter at about 75°. After thorough drying at 100°, the salt when heated slowly loses the remaining molecule of water at about 200° with slight effervescence, and does not then melt until 262° (corr.). If heated quickly, the salt which has been dried at 100° may melt at about 200°. *l*- β -Canadine methochloride is somewhat sparingly soluble in cold water, but very readily so in hot water:

0.9958 air-dried salt lost 0.1854 at 100°. $H_2O=18.6$.

$C_{21}H_{24}O_4NCl, 6H_2O$ requires loss of $5H_2O=18.1$ per cent.

0.1676 * gave 0.3822 CO_2 and 0.0962 H_2O . $C=62.2$; $H=6.4$.

0.1993 * „ 0.4528 CO_2 and 0.1112 H_2O . $C=61.9$; $H=6.2$.

$C_{21}H_{24}O_4NCl, H_2O$ requires $C=61.8$; $H=6.4$ per cent.

* Dried at 100°.

A determination of the specific rotatory power in aqueous solution gave the following result:

$\alpha_D -9.94^\circ$; $c=3.233$ of salt dried at 100° ; $l=2$; $[\alpha]_D -153.8^\circ$, for the monohydrate, which is equivalent to $[\alpha]_D -160.9^\circ$ for the anhydrous salt.

l- β -Canadine methiodide was prepared from the methochloride by double decomposition with potassium iodide. After crystallisation from hot water it formed small prisms, which decomposed at 264° (corr.). This salt is anhydrous, and is very sparingly soluble in water or alcohol:

0.1614 gave 0.3082 CO_2 and 0.0733 H_2O . $\text{C}=52.1$; $\text{H}=5.1$.

$\text{C}_{21}\text{H}_{24}\text{O}_4\text{NI}$ requires $\text{C}=52.4$; $\text{H}=5.0$ per cent.

Conversion of the α - into the β -Form.

It has already been stated that when *l*- α -canadine methiodide is heated above its melting point the liquid first formed becomes crystalline, and does not then melt until about 250° . In order to ascertain with certainty whether the resulting product was *l*- β -canadine methiodide or not, the following experiment was conducted.

A fraction of a gram of *l*- α -canadine methiodide was heated to 230° , and maintained at this temperature for about two minutes. The discoloured product was then dissolved in boiling water decolorised by means of sulphurous acid and animal charcoal, and well shaken with an excess of silver chloride. After filtering from the silver iodide and chloride, the aqueous solution was evaporated to low bulk, when a small quantity of *l*- β -canadine methochloride separated in the typical oblong, colourless prisms, which melted below 100° in the air-dried condition.

Preparation of an Anhydro-base from l-Canadine Methohaloids.

Ten grams of *l*- α -canadine methiodide from *Xanthoxylum brachyacanthum* were dissolved in about 200 c.c. of boiling water, and digested with an excess of silver hydroxide until the solution was free from iodide. After filtering, the strongly alkaline solution of the methohydroxide was evaporated to dryness on the water-bath in an open dish, when an insoluble oil was formed. The residue was then mixed with 100 c.c. of water, and again evaporated to dryness. It was then extracted several times with small quantities of warm water, the extracts being decanted each time from the insoluble, amorphous residue. The latter was then covered with ether, when it immediately began to crystallise; after stirring with ether for a short time, the whole quantity became converted into crystals, which

melted at 105–110°. After one crystallisation from alcohol, 4.1 grams of the anhydro-base were obtained. This base crystallises from alcohol in colourless clusters of needles, which melt at 111–112° (corr.). It is insoluble in water, somewhat sparingly soluble in cold alcohol, but readily so in hot alcohol. It is anhydrous. It behaves as an unsaturated compound towards bromine or permanganate:

0.1813 gave 0.4748 CO₂ and 0.1070 H₂O. C=71.6; H=6.6.

C₂₁H₂₃O₄N requires C=71.4; H=6.6 per cent.

The specific rotatory power of the once crystallised base was $[\alpha]_D -25.2^\circ$, but this gradually diminished with successive crystallisations. A similar result was obtained starting from *l*-β-canadine methochloride, thus affording further confirmation of the identity of the salt from *Xanthoxylum brachyacanthum* with a methyl salt of *l*-canadine.

The optical behaviour of the anhydro-base is of particular interest in connexion with the study of the mechanism of the degradation of tetrahydroberberine by Hofmann's method, and it is proposed to continue the work in this direction.

γ-Homochelidonine from *Xanthoxylum brachyacanthum*.

The crude product previously described (p. 295) was purified by crystallisation from alcohol, when 5.6 grams of the pure base were obtained in stout, colourless needles, which contained half a molecular proportion of alcohol of crystallisation and melted at 170–171° (corr.) after drying at 100°. It is insoluble in water, somewhat sparingly soluble in cold, readily so in hot, alcohol, sparingly so in ether, and readily so in chloroform.

Air-dried base:

Found: C=67.1; H=6.8. Loss at 130°=6.2.

C₂₁H₂₃O₃N, $\frac{1}{2}$ EtOH requires C=67.3; H=6.7; EtOH=5.9 per cent.

Base dried at 130°:

Found: C=68.2, 68.6; H=6.0, 5.7. M.W.=356, 360.

C₂₁H₂₆O₃N requires C=68.3; H=6.3 per cent. M.W.=369.

This base is soluble in dilute acids, and is precipitated by alkali hydroxides, sodium carbonate, or ammonia, but is soluble in a large excess of the latter. It is optically inactive ($c=2.137$ in chloroform; $l=2$ dm.). It neither couples nor forms a nitrosoamine when treated with nitrous acid, and is, therefore, a tertiary base.

It contains a methylenedioxy-group, for on applying Gaebel's test (*Arch. Pharm.*, 1910, 248, 226) a clear red solution is obtained at once, and this becomes turbid when digested in the water-bath.

It contains two methoxyl and one $N\text{-CH}_3$ groups:

0.2014, dried at 130° , gave 0.2572 AgI at $160\text{--}180^\circ$. OMe=16.9;
and 0.1174 AgI at $280\text{--}300^\circ$. NMe=7.2.

$\text{C}_{21}\text{H}_{23}\text{O}_5\text{N}$ requires (OMe)₂=16.8; NMe=7.9 per cent.

The hydrochloride, $\text{C}_{21}\text{H}_{23}\text{O}_5\text{N}\cdot\text{HCl}\cdot\frac{1}{2}\text{H}_2\text{O}$, crystallises from water in colourless, microscopic needles, which have no sharp melting point, but after drying at 100° begin to turn yellow, and sinter at about 165° and effervesce at about 175° (corr.). This salt crystallises with $1\frac{1}{2}$ molecules of water of crystallisation, of which the molecule is lost at 100° . (Found, loss=3.4. Calc., 4.2 per cent. Found, in dried salt, C=60.3; H=6.3; Cl=8.7. Calc., C=60.8; H=6.1; Cl=8.6 per cent.)

The aurichloride, $\text{C}_{21}\text{H}_{23}\text{O}_5\text{N}\cdot\text{HAuCl}_4$, crystallises from alcohol in garnet-red grains, which decompose at 192° (corr.). It is anhydrous, and is very sparingly soluble in water or cold alcohol, but fairly readily so in hot alcohol. (Found, Au=28.0. Calc., Au=27.8 per cent.)

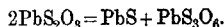
In conclusion, we wish to express our thanks to the Director of the Imperial Institute for suggesting the investigation of the bark, and for a supply of raw material.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

XXXVII.—*The Precipitation of Lead Thiosulphate and its Behaviour on Boiling with Water.*

By WILLIAM HUGHES PERKINS and ALBERT THEODORE KING.

THE formation of lead sulphide when lead thiosulphate is boiled with water is explained in several ways in modern works of reference. On the sole authority of Fogh (*Ann. Chim. Phys.*, 1890, [vi], 21, 56) the reaction is frequently represented by means of the equation:



The present authors, having failed to obtain lead trithionate by this reaction, have examined the data in Fogh's paper, and have come to the conclusion that the above equation has no justification. Apart from the fact that the lead thiosulphate used in the experiments was prepared by a method which probably gave an impure

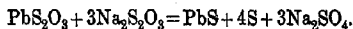
product, the actual experimental data are arithmetically untrustworthy. Starting with 5.087 grams of the thiosulphate, and boiling in a large quantity of water for three hours, Fogh obtained a precipitate which weighed 3.5160 grams, and a filtrate containing both lead and sulphur. On the basis of the above equation, 1.906 grams of sulphide and 3.181 grams of trithionate should be formed. After determining the total lead and total sulphur in both precipitate and filtrate, he expressed his results as follows: The calculated values are obtained from the assumption that the precipitate contains all the lead sulphide (1.906 grams) and 1.610 grams of the trithionate, the remaining trithionate, 1.571 grams, being in the filtrate.

	Precipitate.		Filtrate.	
	Calc.	Found.	Calc.	Found.
Lead	2.490	2.479	0.817	0.809
Sulphur	0.646	0.638	0.213	0.209

On examining these figures it will be observed that the ratio of lead to sulphur in the filtrate does not correspond with that required for PbS_2O_3 , and that, in fact, the calculated quantity of sulphur should be 0.379. This error is so remarkable that it seems reasonable to assume that Fogh calculated the amount of sulphur in 1.571 grams of lead sulphide, which is 0.211 gram. In view of the close agreement between the experimental and the wrongly calculated numbers, it is impossible to base any deduction on the analytical results, and the above equation is without quantitative support.

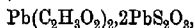
Another equation which is frequently used to describe the change is that suggested from analogy to the similar behaviour of the silver salt, namely, $\text{PbS}_2\text{O}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{PbS}$. The authors have found that only a very slight acidity is developed on boiling for many hours, so that sulphuric acid cannot be assumed to be an essential final product of the reaction. Faktor (*Zeitsch. anal. Chem.*, 1900, **39**, 351) states that the precipitate produced by adding hot concentrated sodium thiosulphate to lead nitrate solution does not blacken, but only turns grey. In the presence of ammonium chloride, however, the blackening is rapid, and he asserts that the precipitate is then composed entirely of lead sulphide. Norton (*Chem. News*, 1901, **89**, 254), who heated lead thiosulphate with water in sealed vessels to over 140° , appears to be the only worker who has recognised the presence of considerable quantities of free sulphur in the black residue. Attention to this fact, together with the observation that the change takes place most readily in the presence of excess of sodium thiosulphate, has led the present authors to the conclusion that the ordinary reaction is best

represented, as far as the initial and final states are concerned, by the equation:



This change may be due to the transformation of a complex ion in solution, because the indications are much less clear in the case of lead thiosulphate alone, although even in this case the products are sulphide sulphate, and free sulphur with small amounts of sulphuric acid, the main reaction being probably analogous to the above, that is, $4\text{PbS}_2\text{O}_3 = \text{PbS} + 4\text{S} + 3\text{PbSO}_4$. It will be seen that both these reactions bear a close resemblance to the usually accepted representation of the decomposition of sodium thiosulphate when heated alone in the absence of air, $4\text{Na}_2\text{S}_2\text{O}_3 = \text{Na}_2\text{S} + 4\text{S} + 3\text{Na}_2\text{SO}_4$.

The trustworthiness of Fogh's data is still more questionable when his method of preparing lead thiosulphate is considered. In the analysis of specimens prepared by precipitation from lead acetate the authors have found that the percentage of sulphur determined gravimetrically and the amount of thiosulphate determined iodometrically are almost invariably lower than those deduced from the formula PbS_2O_3 , and that the discrepancy is caused by the presence of lead acetate. From fairly concentrated solutions using equivalent quantities of lead acetate and sodium thiosulphate, the precipitate is the double salt,



which has previously been obtained in a less direct manner by Lemoult (*Compt. rend.*, 1904, **139**, 422). From more dilute solutions or in the presence of excess of sodium thiosulphate, the precipitate approximates more closely to the simple salt, PbS_2O_3 , but once the double salt has been precipitated it is remarkably stable, and requires prolonged washing with water to effect any change in its composition. For this reason it is unlikely that Fogh, who mixed *N/2*-solutions of lead acetate and sodium thiosulphate,* and did not presumably take any excessive precautions in washing, obtained a precipitate containing 20.1 per cent. of sulphur, which is the theoretical figure for PbS_2O_3 , and the analytical value given in his paper. It must be noted that the percentage of lead is of little value in distinguishing between the two salts, since:

PbS_2O_3 requires Pb=64.85; S=20.10.

$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{PbS}_2\text{O}_3$ requires Pb=64.46; S=13.32 per cent.

Fogh states that from *N/2*-solutions he obtained a filtrate containing only sodium acetate and a precipitate, which contained, after washing, 20.1 per cent. of sulphur. The authors obtained a

* For this purpose a *N*-solution of sodium thiosulphate contains half a gram-molecule per litre. It is, of course, only *N/2* referred to iodine.

filtrate containing a considerable quantity of thiosulphate and a precipitate with less than 17 per cent. of sulphur. The exact nature of the equilibrium between lead acetate, sodium thiosulphate, and water is being made the subject of further inquiry, but it is safe to conclude that the thermochemical and other data and conclusions of Fogh, based on the assumption that his precipitate was pure thiosulphate, are not correct. In the present investigation all specimens of lead thiosulphate for the study of its decomposition were obtained from the nitrate by adding an equivalent quantity of sodium thiosulphate, a process which is found to yield the pure salt.

EXPERIMENTAL.

The Precipitation of Lead Thiosulphate.—12.5 Grams of sodium thiosulphate and 19.0 grams of lead acetate (equivalent quantities) were each dissolved in about 150 c.c. of water, and the solutions mixed. The resulting precipitate was washed by decantation several times, collected, and dried in a vacuum desiccator. It was first analysed by oxidising with bromine, removing the lead sulphate, and then treating the filtrate with barium chloride to obtain the rest of the sulphur as barium sulphate. Owing to the amount of hydrobromic acid produced in the oxidation, the lead was not all precipitated as sulphate, so that the results for lead may be expected to be rather low. As the mean of several analyses we obtained $\text{Pb}=63.54$; $\text{S}=13.33$ per cent. The precipitate is obviously not pure lead thiosulphate ($\text{S}=20.10$ per cent.), but corresponds closely with $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{PbS}_2\text{O}_3$, which only requires 13.32 per cent. of sulphur. As a check on this analysis the iodometric method of Lemoult (*loc. cit.*) was used. The precipitate was dissolved in concentrated potassium hydroxide, the solution diluted, neutralised with sulphuric acid, using phenolphthalein as indicator, and finally titrated with $N/10$ -iodine. In this way it was found that 1 gram of precipitate required 20.5, 20.4, and 20.5 c.c. of $N/10$ -iodine ($\text{S}=13.1$ per cent.). The pure thiosulphate requires 31.3 c.c., and the double salt 20.8 c.c. A specimen of thiosulphate precipitated in a similar manner from lead nitrate gave $\text{Pb}=64.50$ and $\text{S}=20.32$ per cent., and 1 gram required 30.8, 31.0, and 30.7 c.c. of $N/10$ -iodine. In this case the product is practically pure lead thiosulphate. On repeating the precipitation from lead acetate, using very dilute solutions ($N/50$), the precipitation was much slower, and the product, which separated in a crystalline form, gave analytical data which showed that it was nearly pure thiosulphate. One gram required 30.6 c.c. of $N/10$ -iodine ($\text{S}=19.6$ per cent.). A few experiments were carried

out to determine the effect of the concentrations of the reacting solutions, with equivalent quantities and with excess of sodium thiosulphate. As a result, it may be stated that the double salt is precipitated almost pure when solutions more concentrated than about $N/3$ are mixed in equivalent quantities, but that with excess of sodium thiosulphate the tendency to form the double salt is greatly diminished. The double salt, once precipitated, however, is not rapidly decomposed by washing with water, as the following experiment shows. The solutions are of the same concentration as those used by Fogh, although there is no indication that he washed his precipitate so thoroughly. 12.5 Grams of sodium thiosulphate and 19 grams of lead acetate were each dissolved in 200 c.c. of water ($N/2$ -solutions), mixed, and well stirred. The precipitate settled quickly, and the clear liquid, which still contained a great deal of thiosulphate, was poured off and replaced by 300 c.c. of water. This was left in contact with the precipitate for an hour, being stirred repeatedly. This process was repeated five times, and after filtering, the precipitate was dried as before. On analysis 1 gram was found to require 26.2 c.c. of $N/10$ -iodine ($S=16.8$ per cent.), that is, it still contains about one-sixth its weight of lead acetate.

In another experiment 3.841 grams of lead thiosulphate prepared from the nitrate were shaken with about 50 c.c. of N -lead acetate solution. After filtering and drying, the precipitate was found to weigh 5.634 grams, and 1 gram required 20.8 c.c. of $N/10$ -iodine ($S=13.3$ per cent.). Complete formation of the double salt would have been accompanied by an increase in weight to 5.797 grams. The difference is partly due to the appreciable solubility of the double salt.

A corresponding double salt was prepared from lead butyrate by treating a concentrated solution with sodium thiosulphate. The analytical data given by this preparation were:

0.5438 gave 0.4688 $PbSO_4$. $Pb=58.9$.

0.5715 required 11.35 c.c. of $N/10$ -iodine.

$Pb(C_4H_7O_2)_2 \cdot 2PbS_2O_3$ requires $Pb=60.94$ per cent. and 11.2 c.c.

With lead trichloroacetate there appears to be little or no tendency to the formation of a double salt, as the following figures show:

4.140 Grams of anhydrous lead trichloroacetate (3 mols.) were dissolved in a small quantity of water, and 8.36 c.c. of 1.04*N*-sodium thiosulphate (2 mols.) of sodium thiosulphate were added. After allowing to remain, filtering, and washing with a little water the filtrate contained much lead and only a little thiosulphate. The whole of the filtrate required 1.0 c.c. of $N/10$ -iodine, and gave

0.6838 gram of lead sulphate. This corresponds with 1.408 grams of lead trichloroacetate, whereas the amount added in excess of that required for the simple salt was 1.380 grams. 0.2338 Grams of precipitate required 7.30 c.c. of $N/10$ -iodine, that is, 1 gram requires 31.2 c.c. ($S=20.0$ per cent.), corresponding with pure lead thiosulphate.

A precipitate obtained by treating a hot saturated solution of lead formate with one-third of an equivalent of sodium thiosulphate, and rapidly cooling, was pure white, and 0.2301 gram required 7.02 c.c. of $N/10$ -iodine, that is, 1 gram requires 30.5 c.c. ($S=19.6$ per cent.), again obviously pure lead thiosulphate. Apparently only the weak acids which are chemically similar to acetic acid exhibit similar behaviour in this respect.

The Boiling of Lead Thiosulphate with Water.—In an attempt to repeat Fogh's experiment, 5.002 grams of the thiosulphate were boiled with 600 c.c. of water for four hours. A lead acetate paper held in the steam was very slowly blackened, showing that traces of hydrogen sulphide were evolved. After filtering, the filtrate was made up to a litre, and was found to be only slightly acid (100 c.c. required less than 1 c.c. of $N/10$ -alkali), and to contain only very little undecomposed thiosulphate (100 c.c. required only 0.35 c.c. of $N/10$ -iodine). Determinations of lead and sulphur were made in the filtrate, and the dried precipitate was extracted with pure carbon disulphide for the determination of free sulphur. The extracted residue was not found to contain more than small amounts of thiosulphate or of any thionic acid, but was almost entirely composed of sulphide and sulphate. The results of this and other similar experiments are summarised in the following table:

Weight of thiosulphate taken.....	5.002	4.578	2.377
Lead contained (calculated).....	3.247	2.971	1.542
Sulphur „ „	1.003	0.920	0.476
Weight of residue.....	4.441	4.163	2.113
Free sulphur in residue	0.316	0.277	0.125
Combined sulphur in residue	—	0.463	—
Lead in residue	2.999	2.855	1.421
Sulphur in filtrate	0.172	0.137	0.108
Lead „ „	0.198	0.155	0.103
Total sulphur found.....	0.953*	0.877	0.453*
„ lead „	3.197	2.970	1.524

* Assuming the atomic ratio $S : Pb$ in the extracted residue = 1 : 1. In the other experiment this ratio is slightly exceeded.

From these figures it will be seen that the lead is almost completely converted into sulphide and sulphate, and that a considerable amount of free sulphur is liberated. The equation which suggests itself for such a change is $4PbS_2O_3 = 3PbSO_4 + PbS + 4S$, which requires, however, the liberation of half the sulphur in the

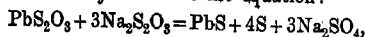
free state. The deficiency in free and in total sulphur, and the large amount of sulphur in the filtrate, are not surprising considering the conditions of the experiment. Sulphur at 100° is appreciably volatile, and acts on water according to the equation $3\text{H}_2\text{O} + 4\text{S} = \text{H}_2\text{S}_2\text{O}_3 + 2\text{H}_2\text{S}$, or in the presence of oxygen: $3\text{H}_2\text{O} + 3\text{S} + \text{O} = \text{H}_2\text{SO}_4 + 2\text{H}_2\text{S}$ (Francis Jones, *Mem. Manchester Phil. Soc.*, 1912, 56, No. XIV).

The excess of combined sulphur in the filtrate is accounted for by the presence of free acid and of polythionates. The filtrates in the above experiments required 16, 8, and 10 c.c. respectively of $N/10$ -alkali for neutralisation. The addition of excess of sodium hydroxide produced in each case a slight turbidity of sulphur, and on keeping for some hours a precipitate of lead sulphide was deposited. Ammoniacal silver nitrate did not give an immediate precipitate, but in a few minutes the black precipitate characteristic of pentathionate was produced.

In order to obtain further information as to the nature of the change, lead thiosulphate or lead nitrate was heated with excess of sodium thiosulphate, when the blackening took place much more rapidly. A weighed quantity of the lead salt was dissolved in a concentrated solution of sodium thiosulphate of known concentration, and the solution sealed up in a glass tube. On warming for a few minutes in a steam-bath a copious, black precipitate was formed. It was first deposited as a mirror on the walls of the tube, and subsequently peeled off. A yellow cloud of sulphur could also be clearly seen. When the action had ceased, the tube was opened, and the precipitate collected. A slight odour of hydrogen sulphide was always observed on opening the tube, but the amount of sulphide in solution was practically negligible. The amount of thiosulphate in the filtrate was determined iodometrically, and the total sulphur present as thiosulphate and sulphate by oxidation with bromine and precipitation as barium sulphate. The free sulphur was extracted from the precipitate by means of carbon disulphide, the residue after this process being in all cases practically pure lead sulphide. In this way the following results were obtained:

1.3110 Grams of lead thiosulphate were heated with 20.0 c.c. of 0.990*N*-sodium thiosulphate. The filtrate after opening the tube was made up to 250 c.c. The precipitate was collected in a tared Gooch crucible, and dried in a desiccator. It weighed 1.506 grams. Twenty-five c.c. of the filtrate required 7.70 c.c. of $N/10$ -iodine, so that 121 c.c. of $N/10$ -sodium thiosulphate had been consumed. This represents 2.92 molecules for each molecule of lead thiosulphate. The weight of sulphur extracted was 0.520 gram, which

is equivalent to 3.96 atoms. The residue after extraction, 0.986 gram, corresponds with 1.00 molecule of lead sulphide. These figures agree remarkably well with the equation:



which also requires three molecules of sodium sulphate in the filtrate. On adding bromine to 25 c.c. of the filtrate and precipitating with barium chloride, the barium sulphate produced weighed 0.6452 gram. The 7.70 c.c. of sodium thiosulphate (*N*/10) account for 0.359 gram, so that there is in the filtrate a quantity of sodium sulphate corresponding with 2.86 grams of barium sulphate. This is 1.747 grams, equivalent to 2.99 molecules per molecule of lead thiosulphate originally taken. This and similar results are collected in the following table, the italics indicating the number of equivalent molecules or atoms of the substance per molecule of lead salt. It will be noted that the numbers obtained by the use of lead nitrate lead to a similar equation.

Weight of lead salt.	C.c. <i>N</i> /10-thio-sulphate consumed.	Sulphur formed.	Lead sulphide.	Sodium sulphate.
1.3110 PbS_2O_3	121.0 (2.94)	0.520 (3.96)	0.986 (1.00)	1.747 (2.99)
1.4533 PbS_2O_3	130.5 (2.86)	0.549 (3.77)	1.077 (0.99)	1.918 (2.96)
1.0885 PbS_2O_3	94.0 (2.89)	0.394 (3.78)	0.748 (0.96)	1.353 (2.93)
0.9887 $\text{Pb}(\text{NO}_3)_2$..	116.0 (3.84)	0.364 (3.77)	0.709 (0.99)	1.292 (3.01)
1.0006 $\text{Pb}(\text{NO}_3)_2$..	118.5 (3.93)	0.370 (3.82)	0.723 (1.00)	1.301 (3.03)

THE UNIVERSITY,
LEEDS.

XXXVIII.—*Ionisation and the Law of Mass Action.*

By WILLIAM ROBERT BOUSFIELD, M.A., K.C.

THE accurate determination of the coefficient of ionisation, even in comparatively dilute solutions, is still a matter of considerable uncertainty. A decisive test as between the various ionisation formulæ which have been proposed is still lacking, and none of the formulæ for "strong" electrolytes has been shown to be in conformity with the principles of the law of mass action. In endeavouring to apply the law of mass action to aqueous solutions, even at moderate dilutions, we are face to face with a very complicated problem. There can be little doubt that there is a progressive hydration of the solute as dilution increases, and that the water itself is a complex substance the proportions of the constituents of which are affected by the nature and amount of the solute; thus, even at moderate dilutions, to apply the law of mass action, we must probably write down at least two reaction

equations belonging to the water itself, and an unknown number of reaction equations expressing the action of the water on the solute in its various stages of hydration. In the region of the highest dilution, when progressive hydration has nearly run its course and has reduced the molecular varieties of the solvent to the fewest possible, and when the proportion of water is so great that its constituents may be regarded as having constant proportions, the mass action problem ought to be reduced to its simplest form. The primary object of the present paper is to determine what is the true ionisation law in the region of highest dilution, so that the fundamental distinction between "strong" and "weak" electrolytes may be clearly enunciated.

In 1902 it was for the first time pointed out (Bousfield and Lowry, *Proc. Roy. Soc.*, 1902, **71**, 48) that the temperature-conductivity curve for "water" practically coincided with the temperature-fluidity curve. The coincidence of the curves revealed the fact that over a very wide range the mobility of the conducting ions was almost exactly proportional to the fluidity, and therefore inversely proportional to the viscosity of the liquid. In 1905 it was pointed out (Bousfield and Lowry, *Phil. Trans.*, 1905, **A**, **204**, 291) that the true coefficient of ionisation for binary electrolytes with univalent ions should be:

$$\alpha = \frac{\lambda}{\lambda_0} \cdot \frac{u_x + v_\infty}{u + v},$$

where λ is the equivalent conductivity and u and v are the true mobilities of the ions, that is, numbers proportional to their actual velocities through the solution under a given potential gradient at the given concentration. It follows that in order to get the true value of α we have to take into account the variation of mobility with dilution. Now the mobility, according to Stokes' Law, should vary, not only inversely as the viscosity of the solution, but also inversely as the radii of the ions, if they can be treated as spherical. It was suggested that as a nearer approximation to the value of α the expression:

$$\alpha = \frac{\lambda \eta}{\lambda_0},$$

should be taken, where η is the viscosity of the solution expressed in terms of the viscosity of water as unity. This correction for the effect of viscosity on the mobility, however, leaves untouched the effect of changes of ionic size, and could not alone be expected to lead to an accurate ionisation formula. Recently endeavours have been made to obtain a further approximation to the true value of α by taking, instead of η , a fractional power of η which is a little less than unity (see Washburn, *J. Amer. Chem. Soc.*, 1911, **33**,

1470). This suggestion leaves out of the account the important considerations which arise from the varying sizes of the ions, and is, in fact, founded on experimental data which ignore such changes. To place the whole correction for α on the viscosity no doubt enables the ionisation formulæ to be moulded in such a way as to give formulæ which are apparently correct over a longer range of dilution, but the theoretical value of the formulæ for elucidating the conditions of mass action and determining the true correction for α is destroyed by such modifications. We must endeavour to get, not an ionisation law which is empirically accurate over a long range, but one which is absolutely accurate in the limiting case of infinite dilution.

Starting, then, with the values of α which are yielded by the expression $\alpha = \lambda\eta/\lambda_\infty$, as our first approximation to the value of α , we must endeavour to get the ionisation law for infinite dilution from the highest range of values in which accurate experimental figures are obtainable, without striving for a formula which comprises the lower range of dilution, where the corrections due to variations of ionic size become more serious. Accuracy in the lower range, whilst the mobility change due to variation of ionic size is uncorrected, will certainly lead us away from the true ionisation law.

Kohlrausch has furnished us with a wonderfully accurate series of conductivity measurements for a number of electrolytes, which go right up to a concentration of $m = 0.0001$. When, however, we proceed to use the figures for the highest concentration as our basis we are met with another difficulty. Kohlrausch, no doubt, used water of very great purity for his solutions, but the effect of the correction for the water conductivity is debatable, and in the necessary manipulation of the solution it is impossible to avoid some change in the conductivity of the water. For $m = 0.0001$ the conductivity of a potassium chloride solution is:

$$\kappa_{18} = 0.00001291.$$

The conductivity of the water used would be of the order:

$$\kappa_{18} = 0.000001.$$

An error of 10 per cent. in the water conductivity would therefore produce an error of 0.8 per cent. in the conductivity and in the value of α . This would produce a much larger error in the value of $(1-\alpha)$, which is the only sensitive factor in ionisation formulæ at high dilution. The divergence of the highest values from the main curve is soon seen when results are plotted. The very high range of dilution where the conductivity of the water introduces obvious errors must therefore be avoided.

Taking both these matters into account, the range of dilution in which we must seek for an ionisation law which shall be accurate at infinite dilution lies between $N/200$ and $N/2000$. With accurate figures between these limits we can avoid the water error and extrapolate with great accuracy past the point where water impurities introduce errors, into the limiting region of "infinite dilution."

We shall illustrate the formulae which it is desired to examine by the figures for potassium chloride. To give detailed figures for other electrolytes would enlarge this communication too much, and is unnecessary, since we are dealing only with principles. In a former paper (Bousfield, *Phil. Trans.*, 1906, A, 206, 155) a proof was given that the van't Hoff dilution law was accurate in the limiting case of infinite dilution. An analogous but simpler proof may now be given. It is convenient in expressing this and other dilution laws to use h , the total number of molecules of water present for one mol. of solute, instead of m or V ; h is, of course, proportional to V at high dilution. The van't Hoff law thus modified becomes:

$$\frac{\alpha^2}{1-\alpha} = Kh^2.$$

For purposes of calculation we may write this as:

$$\frac{3}{2}\log\alpha - \log(1-\alpha) = \frac{1}{2}\log h - C.$$

To test this equation we will take the first approximation figures for the ionisation-coefficient, namely, $\alpha = \lambda\eta/\lambda_\infty$. These values of

Van't Hoff's Law.

TABLE I.

m .	$\alpha = \lambda\eta/\lambda_\infty$.	$y = \frac{3}{2}\log\alpha - \log(1-\alpha)$.	$x = \log h$.	Δy .	Δx .	$\Delta y/\Delta x$.	C .
0.0001	0.9921	2.09721	5.74374	—	—	—	—
0.0002	0.9898	1.98472	5.44271	—	—	—	—
0.0005	0.9847	1.80528	5.04477	—	—	—	—
0.001	0.9738	1.65969	4.74374	0.14557	0.30103	0.4836	0.71712
0.002	0.9709	1.51686	4.44270	0.14283	0.30104	0.4745	0.71218
0.005	0.9562	1.32935	4.04474	0.18751	0.39796	0.4667	0.70449
0.01	0.9440	1.19453	3.74367	0.13482	0.30107	0.4478	0.69363
0.02	0.9218	1.05375	3.44248	—	—	—	—
0.05	0.8891	0.87849	3.04419	—	—	—	—
0.1	0.8600	0.75592	2.74257	—	—	—	—
0.2	0.8276	0.64019	2.44037	—	—	—	—

α for potassium chloride, based on Kohlrausch's figures, are set out in the second column of table I. The third and fourth columns give the values of:

$$y = \frac{3}{2}\log\alpha - \log(1-\alpha)$$

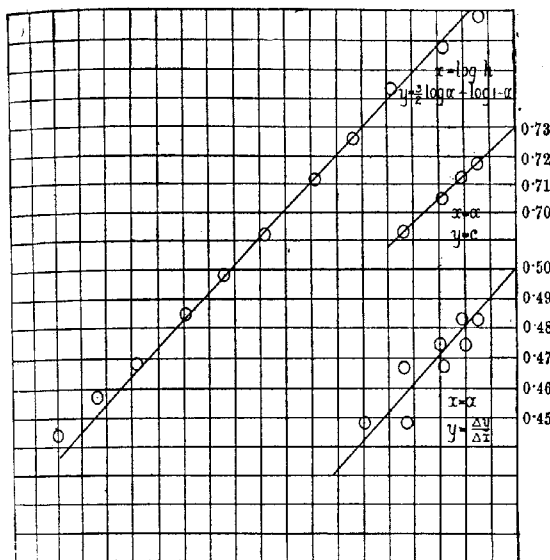
$$x = \log h.$$

These values of y and x are set out in Fig. 1, which shows that the points from $m=0.0005$ to $m=0.005$ give approximately a straight line:

$$y = \frac{1}{2}x - C.$$

To determine the coefficient of x exactly in the region of infinite dilution, the values of Δy and Δx are given in the table, and the values of $\Delta y/\Delta x$ are set out in the diagram on the values of α as abscissæ. They give approximately a straight line law, and show that the limiting value of $\Delta y/\Delta x$ is 0.5. It will be observed that

FIG. 1.



each value of $\Delta y/\Delta x$ is set out twice on the two values of α , one on each side of it. The true position, of course, lies somewhere between the two points, but they are so near as to leave no doubt that 0.5 is the true value of $\Delta y/\Delta x$ at infinite dilution. This is confirmed by taking the value $\frac{1}{2}$ for $\Delta y/\Delta x$ in order to determine what is the limiting value of the constant. For this purpose the values of $y - \frac{1}{2}x = -C$ are calculated and placed in the last column of the table. These are also set out in the diagram on the values of α as abscissæ, giving an excellent line, and showing that the value of C at infinite dilution is 0.730.

By working from the values from $m=0.0005$ to $m=0.005$ we have been able to extrapolate to infinite dilution right past the values where the water error is serious, and we find that the equation which holds as we approach the limit is:

$$\frac{3}{2}\log a - \log(1-a) = \frac{1}{2}\log h - 0.730,$$

which is the van't Hoff law.

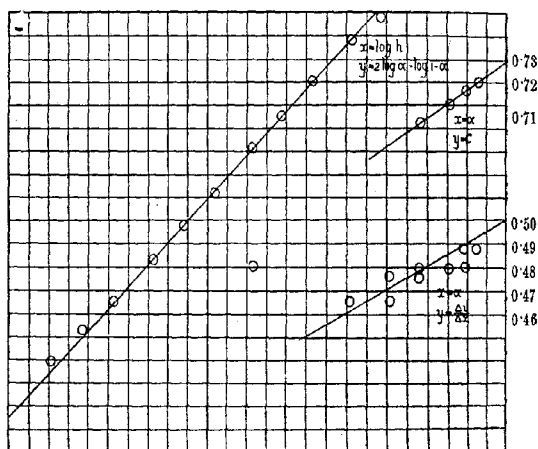
Let us now go through the same process for the Rudolphi law.

Rudolphi's Law.

TABLE II.

m .	$a=\lambda\eta/\lambda_{\infty}$.	$y=2\log a$ $-\log(1-a)$.	$x=\log h$.	Δy .	Δx .	$\Delta y/\Delta x$.	C .
0.0001	0.9921	2.09554	5.74374	—	—	—	—
0.0002	0.9898	1.98250	5.44271	—	—	—	—
0.0005	0.9847	1.80191	5.04477	—	—	—	—
0.001	0.9788	1.65504	4.74374	0.14687	0.30103	0.4879	0.72047
0.002	0.9709	1.51045	4.44270	0.14459	0.30104	0.4803	0.71683
0.005	0.9562	1.31963	4.04474	0.19032	0.39795	0.4795	0.71090
0.01	0.9410	1.17683	3.74367	0.14330	0.30107	0.4760	0.70274
0.02	0.9218	1.03607	3.44248	0.14026	0.30119	0.4657	—
0.05	0.8891	0.85397	3.04419	—	—	—	—
0.1	0.8600	0.72287	2.74257	—	—	—	—
0.2	0.8276	0.59910	2.44037	—	—	—	—

FIG. 2.



The necessary figures are given in table II, and they are all set out in Fig. 2 as before. The same process is gone through, and the result is to give us the Rudolphi equation:

$$2\log a - \log(1-a) = \frac{1}{2}\log h - 0.730.$$

We have then the apparently curious fact that both these

equations are accurately true as we approach the limit of infinite dilution. The reason why they are both true is obviously because in the limit $\alpha=1$, $\log \alpha=0$, and therefore in the limit they both reduce to:

$$-\log(1-\alpha) = \frac{1}{2} \log h - 0.730.$$

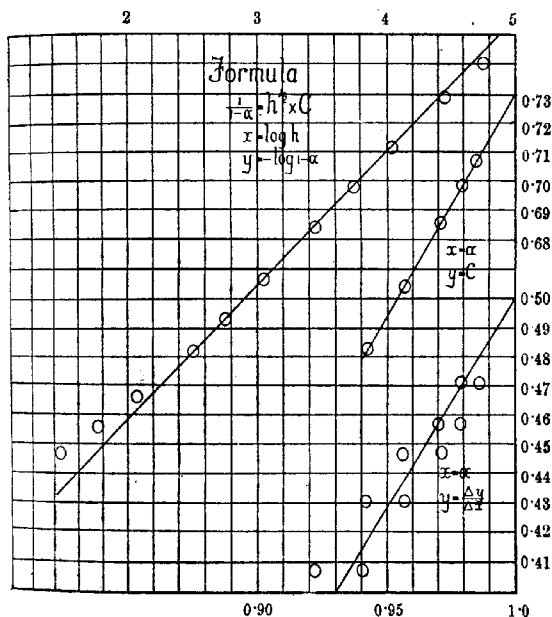
We will now test this new expression in the same way as the two preceding. The necessary figures are given in table III, and

TABLE III.

$$\frac{1}{1-\alpha} = h^{\frac{1}{2}} \times \text{Constant.}$$

m.	$\alpha = \lambda\eta/\lambda_{\infty}$	$y = -\log(1-\alpha)$	$z = \log h$	Δy	Δz	$\Delta y/\Delta z$	C.
0.0001	0.9921	2.10237	5.74374	—	—	—	—
0.0002	0.9898	1.99140	5.44271	—	—	—	—
0.0005	0.9847	1.81531	5.04477	—	—	—	—
0.001	0.9788	1.67366	4.74374	0.14165	0.30103	0.4705	0.7071
0.002	0.9709	1.53611	4.44270	0.13755	0.30104	0.4569	0.6982
0.005	0.9562	1.35853	4.04474	0.17758	0.39796	0.4462	0.6852
0.01	0.9410	1.22915	3.74367	0.12938	0.30107	0.4297	0.6638
0.02	0.9218	1.10679	3.44248	0.12236	0.30119	0.4062	—
0.05	0.8891	0.95507	3.04419	—	—	—	—
0.1	0.8600	0.85387	2.74257	—	—	—	—
0.2	0.8276	0.76346	2.44037	—	—	—	—

FIG. 3.



are set out in Fig. 3. We get as before a straight line with the coefficient 0.5 for x , and the limiting value of the constant the same as before.

Other strong electrolytes of the same class, such, for instance, as sodium chloride and lithium chloride, yield the same exact coefficient 0.5 at infinite dilution, although, of course, the constant differs in each case.

We now see that we can get any number of formulæ of the same form which are equally true in the limit. We may set out the three which have been above investigated, together with two others of the same form which are of some interest:

$$\text{Rudolphi:} \quad \frac{a^2}{1-a} = \frac{h^{\frac{1}{2}}}{5.37}$$

$$\text{Van't Hoff:} \quad \frac{a^{\frac{1}{2}}}{1-a} = \frac{h^{\frac{1}{2}}}{5.37}$$

$$\text{Limiting relation:} \quad \frac{1}{1-a} = \frac{h}{5.37}$$

$$\text{New relation:} \quad \frac{a}{1-a} = \frac{h^{\frac{1}{2}}}{5.37}$$

$$\text{Kohlrausch:} \quad \frac{a^n}{1-a} = \frac{h^{\frac{1}{2}}}{5.37}$$

It will be seen that in the region of very high dilution we can have the index of a anything we please within wide limits. If we make it simply unity we get the new relation which is the fourth above. This particular formula is of interest because we can make it an exact relation down to decinormal dilution by multiplying by the simple exponential factor 10^{1-a} , which gives the equation:

$$\frac{a}{1-a} = h^{\frac{1}{2}} \frac{10^{1-a}}{5.37}.$$

This is an equation which may possibly have a theoretical meaning, and is of practical utility, as it will serve, equally with the Kohlrausch equation, for extrapolation to the value of λ_{∞} .

Having so much flexibility in the index of a , we may choose for the index a value which will make the value of a come out accurate at any given dilution—say, twice decinormal. The required value of the index of a is:

$$n = 3.311.$$

This is the equation used by Kohlrausch for extrapolating to get λ_{∞} . The value of n is slightly different from his value, since we are taking $a = \lambda\eta/\lambda_{\infty}$.

In table IV are set out the values of a obtained from Kohlrausch, from the exponential formula, from Rudolphi, and from van't Hoff. The equations are solved for a by making a table of values

of α for each equation. It will be seen that the Kohlrausch formula gives values which are practically the exact values of $\alpha = \lambda\eta/\lambda_\infty$, the new exponential formula gives these exact values

TABLE IV.
Values of α .

m.	$\alpha = \lambda\eta/\lambda_\infty$	Kohl- rausch.	Diff.	New exponential formula.	Diff.	Rudolphi.	Diff.	van't Hoff.	Diff.
0.0001	0.992	0.992	\pm	0.992	\pm	0.992	\pm	0.992	\pm
0.0002	0.990	0.990	\pm	0.990	\pm	0.990	\pm	0.990	\pm
0.0005	0.985	0.985	\pm	0.985	\pm	0.984	-1	0.984	-1
0.001	0.979	0.979	\pm	0.979	\pm	0.978	-1	0.978	-1
0.002	0.971	0.971	\pm	0.971	\pm	0.970	-1	0.969	-2
0.005	0.956	0.956	\pm	0.956	\pm	0.954	-2	0.952	-4
0.01	0.941	0.941	\pm	0.941	\pm	0.936	-5	0.934	-7
0.02	0.922	0.922	\pm	0.922	\pm	0.914	-8	0.910	-12
0.05	0.889	0.890	+1	0.889	\pm	0.876	-13	0.863	-21
0.1	0.860	0.861	+1	0.859	-1	0.839	-21	0.826	-34
0.2	0.828	0.828	\pm	0.823	-5	0.785	-33	0.776	-52

down to decinormal solutions, the Rudolphi and van't Hoff formulae give values which are within one part in a thousand down to a dilution of $N/1000$ only.

Between these formulae how is one to determine which gives most nearly the true values of α ? One thing is quite clear. The two formulae which give the exact values for $\alpha = \lambda\eta/\lambda_\infty$ cannot be the right formulae for the true value of α , since they leave no margin for the change of α due to the change of mobility which is brought about by variations of ionic size. Empirical correspondences over a long range do not help us, and the only test is to be found by a consideration of other physical properties which depend on α .

In a former paper (Bousfield, *Phil. Trans.*, 1906, A, 206, 101) the matter was approached on the following lines. Starting with the van't Hoff law, which was shown to be true in the limiting case of infinite dilution, and taking the series of values of $\alpha = \lambda\eta/\lambda_\infty$ which correspond accurately with the van't Hoff law in the highest ranges of dilution, it was assumed that the departures of these values of α from those given by the van't Hoff law in the lower ranges of dilution were due to the fact that α was uncorrected for variations of ionic size. It was thus possible, on this assumption, to work out the variations of ionic size which would bring the van't Hoff law into accord with the experimental values of α at such lower dilutions. On this assumption the varying ionic radius was found to be represented by:

$$r = l^{-1}(1 + Bh^{-2})^{-1},$$

where l is the mobility of the ion at infinite dilution. This enabled

the varying volume of the ion to be traced, and hence the varying amount of water combination. It was found that the values of α and of the ionic sizes and of the amounts of combined water thus calculated were concordant with measurements of other physical properties into which these same elements entered. For this purpose the best of these properties is freezing-point depression, since the variation of freezing-point depression values with dilution is correlated to the amount of combined water, so that in this way we get back to change of ionic size, and so to change of mobility due to this cause. Working on these lines, it is shown in the former paper that the variations of ionic size, calculated on the hypothesis that the van't Hoff formula is the right one, do, in fact, lead to values for the combined water which in conjunction with the values of α yielded by the formula are in good accord with experimental determinations of the variations of the freezing-point values with dilution. It will be seen from table IV that the values of α yielded by the Rudolphi formula are practically the same as those given by the van't Hoff formula in the higher ranges of dilution, and only differ from them by two parts in a thousand at a dilution of $N/100$. It follows that the values for the ionic sizes yielded by the Rudolphi formula will not differ greatly in this range from those given by the van't Hoff formula. It remains, however, to examine the values for the ionic sizes which Rudolphi's formula would yield at lower dilutions to see if they are in better or worse agreement with freezing-point depression values and other physical properties—a somewhat delicate and tedious investigation which must stand over for the present. In the meantime as either of these formulæ is in good accord with the variations of freezing-point depressions over a considerable range of dilution, it seems better for various practical purposes to use the values of α derived from one of these two formulæ, rather than to take values of α which are obtained in a more conjectural manner. The matter has been illustrated only by reference to potassium chloride, but these formulæ apply equally, with a change of the constant, to sodium chloride, lithium chloride, and a number of other strong electrolytes.

The difficulty of choice between the formulæ does not, however, meet us in the region of highest dilution. Here all the formulæ which we have examined become the same, and we may say with confidence that in this region there is no doubt about the true relation between ionisation and dilution in this class of "strong" electrolytes. They all reduce to the simple dilution law

$$(1 - \alpha) = k^{-1} \times \text{Constant.}$$

In the same region the Ostwald law for "weak" electrolytes reduces to

$$(1 - \alpha) = h^{-1} \times \text{Constant},$$

Here the mass relation appears in its simplest terms, since in both cases progressive hydration has proceeded so far that molecular varieties have been reduced to the fewest. These two simple formulæ thus bring out the fundamental difference between the class of "weak" electrolytes of which acetic acid is an example, and the class of "strong" electrolytes, of which potassium chloride is an example.

For weak electrolytes the active mass of the undissociated fraction at great dilution is inversely proportional to the mass of the water.

For strong electrolytes the active mass of the undissociated fraction at great dilution is inversely proportional to the square root of the mass of the water.

Here, where the problem is simplest, is the point where reconciliation with the law of mass action as usually enunciated must begin. It is proposed to consider this aspect of the matter in a subsequent paper.

ST. SWITHINS,
HENDON, N. W.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

	PAGE
XXXIX.—Viscosity and Association. Part IV. The Viscosity of the Aromatic Amines. By FERDINAND BERNARD THOLE.	317
XL.—The Reaction between Ferric Salts and Thiosulphates. By JOHN THEODORE HEWITT and GLADYS RUBY MANN.	324
XLI.—Hexahydropyrimidine and its Benzoyl Derivatives. By ARTHUR WALSH TITHERLEY and GERALD EYRE KIRKWOOD.	330
XLII.—The Interaction of Bromine and the Sulphides of β -Naphthol. Part II. By THOMAS JOSEPH NOLAN and SAMUEL SMILES.	340
XLIII.—Researches on the Constitution of Physostigmine. Part II. The Synthesis of 3-Dimethylaminoacetyl-2-methylindole and 2- α -Dimethylamino- γ -hydroxypropylindole. By ARTHUR HENRY SALWAY.	351
XLIV.—Synthetical Experiments in the Group of the <i>iso</i> -Quinoline Alkaloids. Part III. The Constitution of Anhydrocotarnineacetophenone, etc., together with an Account of Some New Condensation Products of Cotarnine. By EDWARD HOPE and ROBERT ROBINSON.	361
XLV.—Contributions to Our Knowledge of Semicarbazones. Part II. Semicarbazones of Mesityl Oxide. By FORSYTH JAMES WILSON and ISIDOR MORRIS HEILBRON.	377
XLVI.—The Chemical Nature of Some Radioactive Disintegration Products. By ALEXANDER FLECK, B.Sc.	381
XLVII.—The Identification of Ipuranol and Some Allied Compounds as Phytosterol Glucosides. By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.	399
XLVIII.—The Absorption Spectra of Substances Containing Labile Hydrogen Atoms. By PETER JOSEPH BRANNIGAN, ALEXANDER KILLEN MACBETH, and ALFRED WALTER STEWART.	406
XLIX.—The Presence of Neon in Hydrogen after the Passage of the Electric Discharge through the latter at Low Pressures. By JOHN NORMAN COLLIE and HUBERT SUTTON PATTERSON.	419

	PAGE
L.—The Double Platinic and Cupric Iodides of Substituted Ammonium Bases. By RASIK LAL DATTA	426
LI.—The Absorption Spectra of Simple Aliphatic Substances in Solutions and as Vapours. Part II. Unsaturated Aldehydes and Ketones. By JOHN EDWARD PURVIS and NIAL PATRICK MCCLELAND	433
LII.—A Novel Method for Resolving Externally Compensated Amines: Derivatives of <i>d</i> - and <i>l</i> -Oxymethylenecamphor. By WILLIAM JACKSON POPE and JOHN READ	444
LIII.—The Mode of Combustion of Carbon. By THOMAS FREDERIC RHEAD and RICHARD VERNON WHEELER	461
LIV.—Existence of Racemic Compounds in the Liquid State. By ALEC DUNCAN MITCHELL and CLARENCE SMITH	489
LV.—The Interaction of Chlorine and Hydrogen. The Influence of Mass. By DAVID LEONARD CHAPMAN and LEO KINGSLEY UNDERHILL	496
LVI.—Quinonoid Salts of Nitroanilines. By ARTHUR GEORGE GREEN and FREDERICK MAURICE ROWE	508
LVII.—The Estimation of Mercury as Metal by the Dry Method. By ALEXANDER CHARLES CUMMING and JOHN MACLEOD	513

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:—

PART I.

Organic Chemistry.

CHABLAY (E.). Some Reactions of Sodamide in the Presence of Liquid Ammonia. Formation of Ethylene Hydrocarbons	i, 241
PAAL (CARL) and CHRISTIAN HOHENEGGER. The Adsorption of Acetylene by Palladium Black	i, 241
BILTZ (HEINRICH). Acetylene or Acetylidene Compounds. The "Oxidation Rearrangement"	i, 241
BHADURI (KSHITIBHUSHAN). Sodium Silver Thiosulphate and Acetylene-Silver Acetylide	i, 241
BASKERVILLE (CHARLES) and H. S. RIEDERER. The Production of Chlorine Substitution Products of Methane from Natural Gas	i, 242
BRAUN (JULIUS VON) and E. DANZIGER. Primary Dinitro-, Nitro-nitrite and Dialdoxime Compounds of the Aliphatic Series. II. Derivatives of the Heptane Series and Synthesis of Pimelaldehyde	i, 242
ENKLAAR (CORNELIS J.). Synthesis of an Unsaturated Hydrocarbon	i, 243
LIPPMANN (EDMUND O. VON). History of Distillation and of Alcohol	i, 243
MOSKALENKO (G.). Action of Magnesium on a Mixture of Ethyl <i>iso</i> -Valerate and Allyl Bromide	i, 244
MICHELIS (LOUIS). Adipipiinacone	i, 244
SCHTSCHERIK (E.). Action of Magnesium on a Mixture of Allyl Bromide and Ethyl Levulinate	i, 244
GRÜN (ADOLF). Synthesis of Lecithin	i, 246
TSCHELINCEV (VLADIMIR T.). Thionium Dibromides of Sulphides	i, 246

CONTENTS.

iii

	PAGE
HAUSER (OTTO) and A. KLOTZ. Catalytic Acceleration of the Esterification of Organic Acid by means of Glucinum Compounds .	i, 246
MICHAEL (ARTHUR) and ERWIN SCHARF. Mechanism of the Action of Bromine on Chlorides of Fatty Acids .	i, 246
STEINKOFF (WILHELM) [with HARRY GRÜNUPF and LEO HUG]. Aliphatic Nitro-compounds. XIII. Preparation of α -Nitro- α -methylbutyric Acid .	i, 246
BOUGAULT (J.) and MOUCHEL-LA-FOSSE. Action of Alkali Sulphites on the Ethylenic Acids .	i, 247
JANTSCH (GUSTAV) and A. GRÜNKRAUT. The Salts of Rare Earths with Hydroxycarboxylic Acids. I. The Glycolates of the Rare Earths .	i, 247
BLAIS (EDMOND E.) and E. CARRIÈRE. Succinic Semialdehyde [β -Aldehydopropionic Acid] .	i, 248
KRISER (EDWARD H.) and L. McMASTER. General Method for the Preparation of the Ammonium Salts of Organic Acids .	i, 248
WHITTEMORE (C. F.) and CHARLES JAMES. Sebacates and Cacodylates of the Rare Earths .	i, 248
GOLDSCHMIDT (GUIDO) and ERNST ZERNER. The Action of <i>p</i> -Bromophenylhydrazine on Glycuronolactone .	i, 249
PALAZZO (F. CARLO) and V. EGIDI. Behaviour of Chloraloxime Towards Water and Alkalis .	i, 249
ROSE (ANTON RICHARD). Inosite-phosphoric Acid .	i, 249
BOURQUELOT (ÉMILE), HENRI HÉRISSEY, and MARC BRIDEL. Syntheses of Alkylgalactosides by means of Emulsin, β -Propylgalactoside and β -Benzylgalactoside .	i, 249
JÖR (WALTHER). Photochemical Synthesis of Carbohydrates .	i, 250
PIEST (C.). Cellulose .	i, 250
BRUN (JULIUS VON) and H. DEUTSCH. Preparation of Higher Aliphatic Chlorinated Amines .	i, 250
SCHELINCEV (VLADIMIR V.). Dibromides of Tertiary Amines .	i, 251
SHOV (ALEXANDER P.). Preparation of Oxan and the Properties of Salts of α - and β -Oxan .	i, 252
EDHOLM (HJ.). Action of Sulphuric Acid on Dicyanodiamide .	i, 252
PALAZZO (F. CARLO). The Tautomerism of Fulminic Acid .	i, 253
MARSHALL (ELI K., jun.), and SOLOMON F. ACREE [and, in part, C. N. MYERS]. Catalysis. XIV. Reversible Addition of Alcohols to Nitriles Catalysed by Ethoxides. I. .	i, 253
KRISER (EDWARD H.) and L. McMASTER. Nitrile of Fumaric Acid and the Preparation of Methyl Maleate .	i, 253
ZERNER (ALEXANDER) and L. GERSTACKER. The Action of Light on Pigments. II. The Composition of Turnbull's Blue .	i, 254
KLINSKI (NICOLAI D.) [with V. KRAVEG, and B. SCHTSCHERRAK]. Spirocyclane, its Synthesis and Behaviour on Catalytic Reduction .	i, 254
BATYER (PAUL) and MARCEL MUBAT. Preparation of the Three Cymenes (Methylisopropylbenzenes) and Three Menthanes (Methylisopropylcyclohexanes) .	i, 255
ERENSHUTKIN (BORIS N.). Systems Formed by Chloro- and Nitro-toluenes with Antimony Trihaloids .	i, 255
LAUS (FRITZ) and LEO LEMMEL. Δ^1 -Dihydronaphthalene .	i, 256
BERG (MOSES). Triphenylmethyl. XXII. Ethers or Oxides in the Triphenylmethane Series .	i, 257
BERG (MOSES). Triphenylmethyl Ether .	i, 259
BITZENBÖCK (RICHARD). Synthesis of Pyrene .	i, 259
BECKER (HERMAN) and PAUL BECKER. Quaternary Salts of Alkylideneamines and a General Method of Converting Primary into Secondary Amines .	i, 260
ALBER (ALPHONSE). The Nitro-derivatives of <i>o</i> -Cresyl Oxide [<i>o</i> -Tolyl Ether] and <i>o</i> -Cresylene Oxide [Di- <i>o</i> -tolylene Oxide] .	i, 261
SCHLAUS (HERMANN). The Action of Aldehydes on Phenols .	i, 261
EDON (M. A.). The Silver Equivalent of Quinol .	i, 262

BAUER (HUGO). <i>o</i> -Nitrophenyl Selenocyanate and <i>o</i> -Aminophenylsalenol	PAGE 1, 261
GAUBERT (PAUL). Some Compounds of Cholesterol giving Liquid Crystals	1, 264
JAKUBOVITSCH (V.). Action of Magnesium on a Mixture of Allyl Bromide and Benzoin	1, 264
RUPE (HANS) and GEORG WOLFSLEBEN. Influence of Constitution on the Rotatory Power of Optically Active Substances. V. Esters of <i>d</i> -Carvoxime	1, 264
LIEBERMANN (CARL). The Determination of the Configuration of the Stereoisomeric Cinnamic Acids	1, 265
LASAUSSIE (ED.). Fixation of the Alkali Hydrogen Sulphites by the Salts and Esters of the Acetylenic Acids	1, 265
GURARIEV (A.). Synthesis of β -m-Tolyl- α -methylhydracrylic Acid	1, 266
RUPE (HANS) [with PAUL HÄUSSLER, EDUARD LENZINGER, and GEORG WOLFSLEBEN]. Influence of Constitution on the Rotatory Power of Optically Active Substances. IV.	1, 266
BOUGAULT (J.). α -Hydroxy- γ -phenylcrotonic Acid. An Example of an Ether of a Ketone Hydrate	1, 269
EGGERER (GRETE) and HANS MEYER. Esters of Aromatic Keto-acids	1, 269
JAROSCHY (STEPHAN). Isomeric Esters of Trichlorobenzoylbenzoic Acids	1, 271
DECKER (HERMAN) [with PAUL BECKER, HEINRICH HOYER, WALTER KROPP, and CLEMENS ZOLLNER]. Preparation of Amides and Acylation of the Amino-group	1, 272
BUTESCU (D.). The Oxidation of Substituted Aceanthrenequinones	1, 273
ORLOY (A.). Action of Magnesium on a Mixture of Allyl Bromide and Phthalic Anhydride	1, 273
JACKSON (C. LORING) and F. C. WHITMORE. The Reaction between 5-Bromo-2:4:6-tri-iodo-1:3-dinitrobenzene and Ethyl Sodiummalonate	1, 273
RIEGER (C. N.). Polymerisation of Cinnamylidenesuccinic Acid by Light	1, 274
CUSMANO (GUIDO). New Oxime of Santonin	1, 277
LIEBERMANN (CARL) and M. KARDOS. The Action of Oxalyl Chloride on Polynuclear Hydrocarbons	1, 27
MENSCHUTKIN (BORIS N.). Compounds of Benzaldehyde and Benzonitrile with Antimony Trichloride and Tribromide	1, 27
MAUTHNER (FERDINAND). New Synthesis of Syringaldehyde	1, 27
GODCHOT (MARCEL) and FÉLIX TABOUREY. α -Chlorocyclopentanone and its Derivatives	1, 27
WALLACH (OTTO) and PAUL FRY. Terpenes and Etheral Oils. CXIII. Autoreduction of Hydroaromatic Compounds at the Moment of their Formation	1, 27
FIGHTER (FRITZ), MAX JETZER, and ROBERT LEEPIN. Synthetic <i>p</i> -Di-alkylated Dihydroxyquinones and Hydroxyperezone	1, 27
BREIT (JULIUS) [with TH. FUSSGÄNGER, J. HOUBEN, P. LEVY, and S. LINKE]. Camphor and its Derivatives. XII.	1, 28
CHOJN (METSCHISLAV). Action of Magnesium and Allyl Haloids on Camphor	1, 28
FRANCESCONI (LUIGI) and E. SERNAGIOTTO. Bupleurol. The Alcohol from the Essential Oil of Bupleurum fruticosum	1, 28
BRADLE (CLAYTON) and HENRY P. STEVENS. Insoluble Constituents of Cera- and Rambong-Caoutchouc	1, 28
HARRIES (CARL D.) [with MAX HAGEDORN, WILHELM SCHÖNBERG and RICHARD SEITZ]. Artificial Caoutchoucs. II.	1, 28
HARRIES (CARL D.) [with MAX HAGEDORN]. Comparative Researches on the Polymerisation Products of β -Dimethylbutadiene obtained Spontaneously and by Heat	1, 28
MARCHLEWAKI (LÉON). Chlorophyll	1, 28
SCHULZE (HEINRICH) and ERICH BIERLING. Alkaloids of <i>Aconitum Lycoctonum</i>	1, 28
DECKER (HERMAN) and THEODOR EICHLER. ψ -Laudanine	1, 28
DECKER (HERMAN), WALTER KROPP, HEINRICH HOYER, and PAUL BECKER. Syntheses of Dihydroisoquinoline Derivatives	1, 28

CONTENTS.

v

	PAGE
BECKER (HERMAN). Syntheses of Hydrastinine and its <i>N</i> -Homologues	i, 290
BECKER (HERMAN) and PAUL BECKER. Synthesis of Cotarnine and Third Synthesis of Hydrastinine	i, 290
BECKER (HERMAN) and PAUL BECKER. Syntheses of Tetrahydroisoquinoline Derivatives	i, 291
BLATT (OSCAR) and PAUL HIRSCH. Synthesis of Pyrroles from Amino-ketones and Ketones or Ketonic Esters	i, 292
LAUFMANN (ADOLF) and LOUIS G. VALLETTE. A New Method of Preparing Cyclamine-aldehydes and -alcohols. II.	i, 293
LAUFMANN (ADOLF), MAX KUNKLER, and HEINRICH PEYER. 4-Quinolyl Ketones. II.	i, 294
TICHT (AME) and B. MANEVITCH. A Methylisophtalisoquinoline	i, 295
LEITER (KURT H.) and HANS SCHLÖSSER. Amino-Imino Desmotropy	i, 295
LOCKMANN (GEORG) and FRANZ LUCIUS. Phenylbenzylidenhydrazine	i, 296
DOMANDUCCI (EZIO). Constitution of "Anilipyrine"	i, 296
CAMPOLLI (LINO METELLO). Constitution of "Anilipyrine"	i, 296
SCHULTZ (GUSTAV) and GEORG RÖHDE. Reaction Products from 1-Phenyl-3-methyl-5-pyrazolone and Phthalic Anhydride	i, 296
JARAPSKY (AUGUST). The Constitution of the Pyrazolincarboxylic Acids	i, 297
BILTZ (HEINRICH) and KARL SEYDEL. A New Example of the Reversed Pinacol Rearrangement	i, 297
KEHRMANN (FRIEDRICH) and EM. HAYAS. Phenazine	i, 298
BRITZENSTEIN (FRITZ) and FRANZ ANDRE. New Methods of Preparation of Asymmetric $\alpha\beta$ -Naphthazine	i, 300
PALAZZO (F. CARLO) and G. MAROGNA. Synthesis of Two Isomeric Oxy-tetrazoles from Azomide and Fulminic Acid	i, 300
WEHNER (S.). Halogen Substitution Products of Azo-dyes	i, 301
BOGDANOVSKI (F. I.). Congo-Red. I. Experimental Part	i, 301
SCHAPOSHNIKOV (VLADIMIR G.). Congo-Red. II. Theoretical Part	i, 301
GREEN (ARTHUR G.) and SALOMON WOLFF. Aniline-Black and Allied Compounds. III.	i, 302
CHICK (MISS HARRIETTE) and CHARLES J. MARTIN. The Density and Solution Volume of Some Proteins	i, 302
PLUMMER (R. H. ADESS). The Hydrolysis of Organic Phosphorus Compounds by Dilute Acid and Dilute Alkali	i, 302
EDDY (WALTER H.). Protein Compounds	i, 302
FISCHER (HANS). Bilirubin and Hæmin	i, 302
HENRIQUES (VALDEMAR) and J. K. GJALDREK. The Action of Pepsin-Hydrochloric Acid on Proteins Partly Digested with Trypsin	i, 302
BERTRAND (GABRIEL), M. ROSENBLATT, and (Mme.) M. ROSENBLATT. Activity of Koji Sucrase [Invertase] in the Presence of Different Acids	i, 302
HENRY (HENRY). Enzymic Decomposition of Glucosides and Galactosides	i, 303
BURGE (W. E.). The Rate of Destruction of Ptyalin by the Direct Electric Current	i, 303
BOUTQUELOT (ÉMILE) and MARC BRIDEL. Resistance of Emulsion to the Action of Heat in Presence of Strong Alcohol	i, 303
FALK (K. GEORG) and MARSTON L. HAMLIN. Enzyme Action. III. Action of Manganous Sulphate on Castor Bean Lipase	i, 303
WARTIC (PERCY) and OTTO STECHE. Enzymic Decomposition of Hydrogen Peroxide. IV.	i, 304
BONGRAND (J. CHARLES). Neutralisation of Solutions of Diaminodihydroxyarsenobenzene Hydrochloride	i, 304
CARRÉ (PAUL). Phenylstibines	i, 304
WOLFF (PAUL). Mercury Dibenzyl	i, 304
POPE (WILLIAM J.). Mercury Dibenzyl	i, 305

Physiological Chemistry.

	PAGE
COOK (FRANK) and MARCUS S. PEMBREY. The Effects of Muscular Exercise in Man	i, 305
HOOKER (DONALD R.). Influence of Calcium and Potassium in the Respiratory Rhythm in Frogs	i, 305
BURN (J. H.). The Oxygen Capacity of Blood in Relation to the Concentration of Hemoglobin	i, 306
BARCROFT (JOSEPH) and J. H. BURN. Determination of the Constant of the Differential Blood-Gas Apparatus and the Specific Oxygen Capacity of Blood	i, 306
BARCROFT (JOSEPH), R. A. PETERS, FR. ROBERTS, and J. H. RYFFEL. The Effect of Exercise on the Dissociation Curve of Blood	i, 306
BARCROFT (JOSEPH), MARIO CAMIS, G. C. MATHISON, FR. ROBERTS, and J. H. RYFFEL. The Effect of Altitude on the Dissociation Curve of Blood	i, 306
BARCROFT (JOSEPH), G. GRAHAM, and HAROLD L. HIGGINS. The Effect of Carbohydrate-free Diet on the Dissociation Curve of Blood	i, 306
BARCROFT (JOSEPH), MARIO CAMIS, G. C. MATHISON, FR. ROBERTS, and J. H. RYFFEL. The Effect of Moist Heat on the Dissociation Curve of Blood	i, 306
LÉPINE (RAPHAËL) and RAYMOND BOCLUD. Sugar Loosely Combined in the Blood	i, 307
ROLLY (FR.) and FR. OPPERMANN. The Behaviour of Blood-Sugar in Normal and Pathological Cases. IV. The Blood-Sugar in Febrile and Dyspnoic Conditions of Man	i, 307
ROLLY (FR.) and FR. OPPERMANN. The Behaviour of Blood-Sugar in Normal and Pathological Cases. V. The Blood-Sugar in Nephritis, Arteriosclerosis, and Diseases of the Nerves	i, 307
BARRATT (J. O. WAKELIN). Fibrinsemia	i, 308
RONA (PETER) and PAUL GYÖRGY. The Sodium and Carbonate Ions in the Serum, and the Question of the "Non-diffusible" Alkali	i, 308
O'BRIEN (R. A.). Rate of Regeneration of Anti-substances [Specially Hemolysin] and Other Constituents of the Blood after Hæmorrhage	i, 308
RITCHIE (JAMES) and J. MILLER. Can Lipoids Act as Antigens?	i, 308
NORRIS (ROLAND VICTOR). Hydrolysis of Glycogen by Diastatic Enzymes. Comparison of Glycogen from Various Sources	i, 308
MATSUO (IWAWO). The Secretion of Pancreatic Juice	i, 309
WEED (LEWIS H.), HARVEY CUSHING, and CONRAD JACOBSON. The Role of the Pituitary in Carbohydrate Metabolism	i, 309
FLEMING (G. B.). Carbohydrate Metabolism in Ducks	i, 309
ABDERHALDEN (EMIL) and ARNO ED. LAMPÉ. Nitrogen Retention on Feeding with Urea	i, 310
FOLIN (OTTO) and W. DENIS. Protein Metabolism from the Point of View of Blood and Tissue Analyses. VI. Uric Acid, Urea, and Total Non-protein Nitrogen in Blood	i, 310
PLIMMER (R. H. ADERS). The Metabolism of Organic Phosphorus Compounds; Their Hydrolysis by the Action of Enzymes	i, 310
CATHCART (E. PROVAN) and HENRY HAMILTON GREEN. The Rate of Protein Katabolism	i, 311
MELLANBY (EDWARD). The Metabolism of Lactating Women	i, 311
BYWATERS (HUBERT W.). Nutrition of the Embryonic Chick. I. The Absorption of Egg-white	i, 311
DURLACH (ERNST). The Importance of Phosphorus in the Nutrition of Growing Dogs	i, 311
OSBORNE (THOMAS B.) and LAFAYETTE B. MENDEL. Nutritive Value of the Maize Proteins	i, 312
HOPKINS (F. GOWLAND) and ALLEN NEVILLE. The Influence of Diets upon Growth	i, 312

CONTENTS.

vii

	PAGE
HOWE (PAUL E.). Fasting	i, 312
ROSENBLOOM (JACOB). A New Method of Drying Tissues and Glands	i, 312
HARVEY (E. NEWTON). A New Type of Artificial Cell	i, 312
ESCHER (HEINRICH H.). Pigment of the <i>Corpus luteum</i>	i, 312
SMITH (J. LORRAIN) and W. MAIR. The Lipoids of the White and Grey Matter of the Human Brain at Different Ages	i, 313
TASHIRO (SHIRO). Chemical Changes in Nerve During the Passage of a Nerve Impulse	i, 313
MACLEAN (HUGH) and (Miss) IDA SMEDLEY. The Utilisation of Sugars by the Normal Heart	i, 313
MACLEAN (HUGH) and (Miss) IDA SMEDLEY. The Behaviour of the Diabetic Heart towards Sugar	i, 313
ISHIMORI (KUNIOMI). The Storage and Release of Glycogen	i, 313
LIU (HANS). The Character of the Fat Formation in Organs after Phosphorus Poisoning	i, 314
LEO (HANS) and W. TRASCHENNIKOV. Fat Formation under the Influence of Phosphorus	i, 314
LEO (HANS) and C. BACHEM. Fat Formation in the Surviving Liver	i, 314
HILL (ARCHIBALD V.). The Delayed Heat-Production of Muscles Stimulated in Oxygen	i, 314
BERG (WILLIAM N.). The Physico-chemical Basis of Striated Muscle Contraction. II. Surface Tension	i, 314
BEUTNER (REINHARD). Osmotic and Colloidal Imbibition by Muscle	i, 315
GRUND (GEORGE). The Chemical Pathology of Muscle. The Influence of Disuse Atrophy in the Partition of Nitrogen and Phosphorus in the Muscle	i, 315
MYERS (VICTOR C.) and MORRIS S. FINE. The Creatine Content of Normal Muscle and its Relation to Urinary Creatinine	i, 315
KORNFELD (FRIEDRICH). Occurrence of Alizarin in the Shell of the Crab	i, 315
LABAT (A.). Normal Presence of Bromine in Human Organs	i, 315
BERTRAND (GABRIEL) and FLORENTIN MEDIGHECEANU. The Presence and Distribution of Manganese in Animal Organs	i, 316
WEGŻYŃSKI (LESŁAW). The Origin of Oxalic Acid in the Animal and Human Organism	i, 316
PATEIN (GEORGES). Histones and Nucleohistones. Their Detection in the Fluids of the Organism	i, 316
GESELL (ROBERT A.). Relation of Pulse Pressure to Renal Secretion	i, 316
PILCHER (J. D.). Excretion of Nitrogen after Ligaturing the Renal Arteries	i, 317
FUNK (CASIMIR). Beri-Beri. The Action of Certain Purine and Pyrimidine Derivatives	i, 317
KAHN (MAX) and JACOB ROSENBLOOM. Colloidal Nitrogen in the Urine of a Dog with a Breast Tumour	i, 317
ROBIN (ALBERT). The Comparative Mineralisation of Cancerous and Relatively Healthy Portions of the Liver	i, 317
WHIPPLE (GEORGE H.). Hematogenous Jaundice	i, 317
HAUBERRISSEK (EDWIN) and FRITZ SCHÖNFELD. The Swelling of Connective Tissues	i, 318
ELLIS (RALPH S.). Antagonism between Salts and Anæsthetics. III. Parallel Decrease in the Stimulating, Permeability-increasing, and Toxic Actions of Salt Solutions in the Presence of Anæsthetics	i, 318
BUCHTALA (HANS). Behaviour of Mercury in the Human and Animal Organism on the Usual Therapeutic Methods of Application. New Method for the Estimation of Mercury in Urine and in the Tissues	i, 318
HYDE (IDA H.), RUTH SPRAY, and IRENE HOWAT. The Influence of Alcohol on Reflex Action in the Frog	i, 318
RINGER (A. I.) and L. JONAS. Glyconeogenesis. II. The Formation of Dextrose from Valeric and Hepticoic Acids	i, 319
EWINS (ARTHUR J.) and PATRICK P. LAIDLAW. The Fate of Indole-ethylamine [3- β -Aminocethylindole] in the Organism	i, 319

	PAGE
ROSENBLUM (JACOB) and WILLIAM WEINBERGER. Influence of Intraperitoneal Injection of Adrenaline on the Partition of Urinary Nitrogen in a Dog	i, 319
JACKSON (DENNIS E.). Action of Drugs on the Lungs	i, 319
HANDOVSKY (HANS) and ERNST P. PICK. The Pharmacological Susceptibility of the Peripheral Vascular Tonus of the Frog	i, 319
BURRIDGE (W.). Nicotine and Calcium Salts	i, 320
MELTZER (SAMUEL J.). The Effect of Strychnine on Frogs without Heart and Lymph Hearts	i, 320
QUAGLIARIELLO (G.). Muscle Physiology. Action of Veratrine on Striated Muscles in Warm-blooded Animals	i, 320
LEHMANN (KARL B.) and LUDWIG DIEM. The Action on Man of Vapours of Technical and Hygienic Importance. XXX. Nitric Acid	i, 320
LEHMANN (KARL B.) and HASEGAWA. The Action on Man of Vapours of Technical and Hygienic Importance. XXXI. The "Nitrous Gases": Nitric Oxide, Nitrogen Dioxide, Nitrous and Nitric Acids	i, 320
WILLBERG (M. A.). The Natural Resistance of the Hedgehog towards Certain Poisons	i, 321

Chemistry of Vegetable Physiology and Agriculture.

SALKOWSKI (ERNST). Bacterial Reduction of Sulphates to Sulphides	i, 322
FRANZEN (HARTWIG) and F. EGGER. Bio-chemistry of Micro-organisms. VII. The Fermentation of Formic Acid by <i>Bacillus Kiliense</i> in a Medium of Constant Composition	i, 322
AGULHON (HENRI) and ROBERT SAZERAC. Action of Uranium Salts and Metallic Uranium on the Pyrocyanic Bacillus	i, 322
BEQUEREL (PAUL). Influence of Salts of Uranium and Thorium on the Development of Tubercle Bacillus	i, 322
ZIFFEL (HUGO). Indole Reaction	i, 323
KOSTYTSCHEV (S.). Mechanism of Alcoholic Fermentation	i, 323
KOSTYTSCHEV (S.). Alcoholic Fermentation. III. Conditions Regulating the Formation of Acetaldehyde during the Fermentation of Hefanol (Yeast)	i, 323
BOUQUELOT (EMILE), HENRI HÉRISSEY, and MARC BRIDEL. Biochemical Synthesis of Alkylglucosides (α -Glucosides) by means of a Ferment (α -Glucosidase) contained in Air-dried Bottom Yeast. α -Ethylglucoside	i, 323
BAUDRICH (OSKAR) and EDWIN MAYER. Assimilation of Nitrate and Nitrite. V.	i, 324
STOKLASA (JULIUS). The Influence of Uranium and Lead on Vegetation	i, 324
BOROVNIKOV (G. A.). The Cause of Growth in Plants. I.	i, 324
ANGELICO (FRANCESCO) and G. CATALANO. Presence of Formaldehyde in the Sap of Green Plants	i, 325
ZALERKI (W.) and ELIZABETH MARX. The Function of the Carboxylase in Plants	i, 325
KEEBLE (FREDERICK) and EDWARD FRANKLAND ARMSTRONG. Role of Oxydases in the Formation of the Anthocyan Pigments of Plants	i, 325
IVANOVSKI (D.). Colloidal Chlorophyll and the Shifting of the Absorption Bands in the Leaves of Living Plants	i, 326
THOMAS (CARL). Plant Fats	i, 326
LEPIERRE (CHARLES). The Non-Specificity of Zinc as a Biological Catalyst for the culture of <i>Aspergillus niger</i>	i, 326
JAVILLIER (MAURICE). Attempts to Substitute Glucinum for Magnesium and Zinc in the Culture of <i>Sterigmatocystis niger</i> (<i>Aspergillus niger</i>)	i, 326
LEPIERRE (CHARLES). Replacement of Zinc by Glucinum in the Culture of <i>Aspergillus niger</i>	i, 327
FOSSE (ROBERT). Formation of Urea by Two Moulds	i, 327
FUNK (CASIMIR). The Nitrogenous Constituents of Lime Juice	i, 327

CONTENTS

ix

	PAGE
THOMAS (CARL). Constituents of Apples	i, 327
JENSEN (HAROLD R.). Leaves of <i>Barosma venusta</i>	i, 328
BLANKSMA (JAN J.). Constituents of <i>Lycoperdon bovista</i>	i, 328

PART II.

General and Physical Chemistry.

ROSS (P. A.). Refractive Index of Metals	ii, 165
MAZZUCHELLI (ARRIGO). Further Remarks on a Formula for the Index of Refraction of Binary Mixtures	ii, 165
FÖRSTERLING (K.) and VASVOLOD FRÉDERICKSZ. Optical Constants of Certain Metals in the Ultra-Red	ii, 165
MEUNIER (JEAN). The Spectra of Nebulae and the Analogies to be Drawn from Them	ii, 165
STREUBING (WALTER). Influence of Different Gases and of Variations in Gas Pressure and Current Strength on the Appearance of the First Ultra-violet Band Spectrum of Oxygen	ii, 166
STARK (JOHANNES). Systems of Series in the Spectra of Zinc, Cadmium, and Mercury	ii, 166
MAZZUCHELLI (ARRIGO) and OLGA GRECO D'ALCEO. Absorption Spectra of Some Uranyl Salts	ii, 167
MEYER (RICHARD) and OTTO FISCHER. Spectrographic Studies in the Triphenylmethane Group	ii, 167
MEYER (RICHARD) and OTTO FISCHER. Spectrographic Studies in the Anthraquinone Group	ii, 168
CAIN (JOHN C.). Optical Investigation of Diazo-compounds	ii, 169
LEY (HEINRICH) and W. FISCHER. Absorption of Light and Fluorescence of Aliphatic Acid Imides (Fluorescence Phenomena among Non-aromatic Compounds. I.)	ii, 169
LIEBIG (HANS VON). Stark's Theory of Fluorescence	ii, 170
HENRI (VICTOR) and RENÉ WURMSER. The Law of Elementary Photochemical Absorption	ii, 171
BOLL (MARCEL). Relation between the Velocity of a Photochemical Reaction and the Incident Radiant Energy	ii, 171
BRETHERLOT (DANIEL) and HENRY GAUDECHON. Action of the Medium and Extreme Ultra-violet Rays on Acetaldehyde: Acidification, Polymerisation, Resinification	ii, 171
ALLEN (H. STANLEY). Photo-electric Behaviour of Iron in the Active and Passive State	ii, 172
HUGHES (A. LL.). Photo-electric Effect in Some Compounds	ii, 172
STARK (JOHANNES). Arc and Spark Lines (Uni- and Multi-valent Lines) in the Canal-Ray Spectra	ii, 172
WILSAR (HEINRICH). Doppler Effect of Canal Rays	ii, 172
CHAPMAN (J. CROSBY). Comparison of the Spectra of Fluorescent Röntgen Radiations	ii, 173
FRANCK (J.) and G. HERTZ. Measurement of the Ionisation Potential in Different Gases	ii, 174
COSTANZO (GIOVANNI). The Occlusion of the Products [of Disintegration] of Radium	ii, 174
HEVEY (GEORG VON). The Valency of the Radio-elements	ii, 174
HEVEY (GEORG VON) and L. VON PUTNOKY. The Diffusion of Uranium	ii, 175
MICHELIS (L.). The Radioactivity of Solutions of Uranium Salts	ii, 176
LA ROSA (M.). Change in Activity of a Sample of Uranium Nitrate	ii, 176
ROSSI (PAOLO). Behaviour of Uranium-X with Regard to the Usual Methods of Electrochemical Separation	ii, 176

	PAGE
MUÑOZ DEL CASTILLO (JOSÉ) and JOSÉ BARRIO FERNÁNDEZ. Synthetic Observations on the Activity of Rain Water	ii, 177
LAUB (J.). The Atmospheric Electricity and Radioactivity of the Atlantic and Pacific Oceans. I. Determination of the Emanation Content of Ocean Water	ii, 177
CHRISTIANSEN (CHRISTIAN). Electrical Excitation in the Spraying of Liquids (Ballo-electricity). II.	ii, 177
WASHBURN (EDWARD W.) and J. E. BELL. Improved Apparatus for Measuring the Conductivity of Electrolytes	ii, 177
FISCHLER (J.). The Molecular Conductivity and Viscosity in Mixtures of Methyl Alcohol or Acetone with Benzene and Nitrobenzene	ii, 178
GOLDSCHMIDT (FRANZ) and LÉON WEISSMANN. Aqueous Solutions of Ammonia Soaps. I.	ii, 178
PLOTNIKOV (VLADIMIR A.). Electrochemistry of Non-aqueous Solutions. X. Schützenberger's Etherobromide	ii, 179
GUYOT (J.). The Apparent Potential Difference of Contact of a Metal and Electrolytic Solutions	ii, 180
KREMMANN (ROBERT) and FELIX NOSS. Theory of the Skinner-Case Electrolytic Thermo-element, $\text{Sn}(\text{CrCl}_3)\text{Pt}$, and on Other Elements of Analogous Type	ii, 180
COHEN (ERNST). The Influence of High Pressures on Faraday's First Law	ii, 181
SCAGLIARINI (GINO) and A. CASALI. Anodic Oxidation of Ammonia in an Acid Liquid in the Presence of Silver Salts	ii, 181
NAMÉ (RALPH G. VAN) and CARLTON H. MARYOTT. The Mechanism of the Chlorination of Benzene in the Electrolytic Cell	ii, 181
BOLL (MARCEL). Measurement of the Energy of the Ultra-violet Radiation Emitted by an Arc in Mercury Vapour under Different Conditions	ii, 182
ROMANOV (W.). Selective Absorption of Electromagnetic Waves	ii, 182
PASCAL (PAUL). The Additivity of Diamagnetism in Compounds	ii, 182
ALBERTHUM (HANS). Relative Scale of Temperature for Solid Substances	ii, 183
SCHERL (KARL) and WILHELM HEUSE. Specific Heat of Helium and Certain Diatomic Gases between 2° and -180°	ii, 183
RICHTER (OSKAR). Influence of the Free Electrons on the Specific Heat of Metals and Alloys	ii, 184
RICHARZ (FRANZ). [Law of Dulong and Petit]	ii, 184
AMAGAT (ÉMILE H.). Internal Pressure in Fluids	ii, 185
KÖRBER (FRIEDRICH). Melting Curves of Stable and Metastable Crystalline Substances	ii, 185
LEDUC (ANATOLE). Latent Heats of Vaporisation and Maximum Pressures	ii, 185
MEISSNER (WALTHER). Constancy of the Boiling Point of Sulphur	ii, 185
RUSS (FRANZ) [with ERNST EBERWEIN]. The Vapour-pressure Curve of Nitrogen Tetroxide	ii, 186
REED (WALTER W.). Simple Demonstration of the Lowering of Vapour Pressure	ii, 186
HACKER (CARL). Variation of the Vapour Pressure of Aqueous Sulphuric Acid Solutions with the Temperature	ii, 189
ROTH (WALTER A.) and GUSTAF JIM ÖSTLING. Thermochemical Investigations in the Alicyclic Series	ii, 187
AMAGAT (ÉMILE H.). The Laws of Corresponding States	ii, 188
DUCLAUX (JACQUES). The Elements of Energy	ii, 188
BATSHINSKI (ALEXIS J.). The Molecular Association of Liquids. I.	ii, 188
BATSHINSKI (ALEXIS J.). The Molecular Association of Liquids. II.	ii, 188
ANDRÆE (J. L.). A Method for the Determination of the Density of Solid Substances	ii, 189
KLOOSTER (H. S. VAN). Normal and Abnormal Cases of Specific Volume of Binary Liquid Mixtures	ii, 189
HANSEN (G. HIRSCHFELDT). A Relation between the Atomic Volumes of the Elements and their Power of Forming Complex Compounds	ii, 189
SCHWABE (H.). Viscosity and its Significance for the Chemistry of Celluloid in Theory and Practice	ii, 189

CONTENTS.

xi

	PAGE
SCHMIDT (FRIEDRICH). Change of the Surface Tension of Mercury on the Addition of Metals	ii, 190
KURNAKOV (NIKOLAI S.) and S. F. SHEMITSCHVSHNI [with A. ARSENEV and V. ZELIGER]. Internal Friction of Binary Systems. Characteristics of Definite Compounds	ii, 190
SCHARFER (CL.) and G. FRANKENBERG. Influence of Temperature on the Turbulent Flow	ii, 191
MIR (GUSTAV). Turbulence Viscosity	ii, 192
SCHULTZE (GÜNTHER). Determination of the Degree of Dissociation of Molten Silver Chloride and Silver Bromide	ii, 192
BOGDAN (PETRU). Method of Calculation of the Constant of Capillarity. The Eötvös-Bainy Rule. The Coefficient of Compressibility of Liquids	ii, 192
LAAR (JOHANNES J. VAN). The Theory of Osmotic Pressure	ii, 193
GIES (WILLIAM J.), JACOB ROSENBLUM, WILLIAM H. WELKER, GEORGE D. BEAL and GEORGE A. GEIGER. Diffusion through Rubber Membranes	ii, 193
BRILLOUIN (MARCEL). General Characters of the Actions between Molecules	ii, 193
BAUD (ÉMILE). The Partial Miscibility of Liquids	ii, 193
TAMMANN (GUSTAV). The Atomistic Theory of Polymorphism	ii, 193
ZSIGMONDY (RICHARD) and WILHELM BACHMANN. Jellies	ii, 194
ODÉN (SVEN) and E. ÖHLON. Reversible Coagulation Processes	ii, 194
DOMANSKI (A.), E. ZABOTINSKI, and M. EVSEEV. Method for the Determination of the Size of Colloidal Particles	ii, 194
OSTWALD (WOLFGANG). The Application of the Principles of Colloidal Chemistry to the Considerations of the Question of Specificity	ii, 195
JÄNCKE (ERNST). Reciprocal Salt Pairs and Double Ternary Salt Mixtures	ii, 195
SCHREINEMAKERS (FRANS A. H.). The Partial Pressures of Ternary Mixtures	ii, 196
SCHREINEMAKERS (FRANS A. H.). The Quadruple Point and Triple Curves in Binary Systems	ii, 196
COPPADORO (ANGELO). The Equilibria in the System Barium Chloride, Sodium Nitrate, Barium Nitrate, Sodium Chloride, and Water	ii, 196
NANTY (T.). Equilibria between Potassium Hydrogen Carbonate and Salts of Magnesium, Nickel, and Cobalt	ii, 196
BIDET (FÉLIX). Displacement of the Primary Amylamines by Gaseous Ammonia	ii, 197
SEUTYEV (B.). Influence of Temperature on the Velocity of Chemical Reactions. II.	ii, 198
VORLÄNDER (DANIEL) and WALTER STRUBE. The Action of Carbonic Acid on Alkalis and Alkaline Earths as a Time Reaction	ii, 198
THIEL (ALFRED). The Slow Neutralisation of Carbonic Acid	ii, 199
JUST (GERHARD) and YRÖ KAUKO. Kinetic Investigation of the Action of Carbon Monoxide on Solutions of Potassium Permanganate	ii, 199
RÖNA (ELISABETH). The Velocity of the Reaction of Bromine and Aqueous Solutions of Monohydroxy-Aliphatic Alcohols	ii, 199
WAGNER (CARL L.). Gradual Hydrolysis	ii, 200
PERKOV (NICOLAS VON) and JULIUS MEYER. Saponification in Stages. III. Hydrolysis of Acid Amides and Nitriles	ii, 201
RIVET (ALBERT C. D.). The Dynamics of the Change Aceto-chloroanilide \rightarrow <i>p</i> -Chloroacetanilide in the Presence of Acids	ii, 202
JABŁCZYŃSKI (KASIMIR). Velocity of Formation of Precipitates	ii, 203
BOULANGÉ (CH.) and GEORGES URBAIN. Theory of the Efflorescence of Saline Hydrates. Influence of Temperature	ii, 203
MEYER (KURT H.). Velocity of Reaction and Catalysis	ii, 204
ROSENROFF (MARTIN A.). Outline of a Theory of Homogeneous Catalysis	ii, 204
POSE (WILLIAM A.). Surface Combustion	ii, 204
ABEL (ÉMILE). Catalytic Studies. II. Barium Iron Catalysis	ii, 204
NIEDLINGER (SIDNEY), F. M. ROGERS, and SOLOMON F. ACHER. Catalysis XIII. Reaction of Ethyl Iodide with Sodium; 3-Thio-1-phenylurazole	ii, 205

	PAGE
BILECKI (ALDIS). The Periodic System and Atomic Weight	ii, 205
JUNGFLEISCH (ÉMILE). The Life and Work of Marcellin Berthelot	ii, 205
BAKER (ROSS ALLEN). Substitution of Ground Glass Stopper in Combination Barometer and Manometer	ii, 205
BAKER (ROSS ALLEN). New Cover Glass Support	ii, 206
SHEDDEN (FRANK). A Simple Form of Gas Generator	ii, 206
MICHEL (FRANZ). A New Reflux and Distillation Condenser	ii, 206
PRANDTL (WILHELM). Two Lecture Experiments on the Diamond	ii, 206
MCDERMOTT (F. ALEX.). Reaction between Calcium Permanganate and Ethyl Alcohol	ii, 207
KURNAKOV (NIKOLAI S.) and N. N. EFREMOV. Lecture Experiments Showing the Formation of Binary Liquid Eutectics	ii, 207

Inorganic Chemistry.

VANINO (LUDWIG) and A. SCHINNER. A New Hydrogen Table	ii, 207
WAHL (WALTER). Optical Investigation of Solidified Gases. II. Crystallographic Properties of Hydrogen and Oxygen	ii, 208
BIEBER (WILLIE). Condensation of Water Vapour in Presence of Oxides of Nitrogen and of Hydrogen Peroxide. Evidence of the Formation of Hydrogen Peroxide by Oxidation of Water Vapour. Action of Ultraviolet Sunlight on the Earth's Atmosphere	ii, 208
CHATTAWAY (FREDERICK D.). The Preparation of Anhydrous Hydrofluoric Acid and the Isolation of Fluorine	ii, 209
LANGMUIR (IRVING). Chemical Reactions at Very Low Pressures. I. The Clean-up of Oxygen in a Tungsten Lamp	ii, 209
MOLES (ENRIQUE) and SANTIAGO PIÑA DE RUBIES. The Presence of Selenium in Hydrochloric Acid	ii, 209
COMTE (F.). The "Chemically Active Modification" of Nitrogen	ii, 210
TIEDT (ERICH). Active Nitrogen	ii, 210
MENEGHINI (D.). Catalytic Oxidation of Ammonia. II.	ii, 210
KOENIG (ADOLF). Chemistry of the Formation of Nitric Oxide in the High Tension Arc	ii, 210
BRINER (EMIL) and BOUENOFF. Chemical Reactions in Compressed Gases. Decomposition of Nitric Oxide	ii, 210
SCHMIDT (HANS). The Luminescence and Ionising Action of Inactive Gases Saturated with Phosphorus Vapour	ii, 211
TAUCHERT (FRITZ). The Formation of Hypophosphoric Acid in Corne's Reaction	ii, 211
REYNOLDS (J. EMERSON). The Synthesis of a Silicocyanide and of a Felspar	ii, 212
BASCHIERI (ENNIO). Tschermak's Method for the Isolation of Silicic Acids	ii, 213
AMADORI (MARIO). Tendency of Haloids and Phosphates of the Same Metal to Combine. II. Alkali Fluorides and Phosphates	ii, 213
SBORGI (U.). Borates. The System $(\text{NH}_4)_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 30°	ii, 213
CAMBI (LIVIO). Silver Thioaluminates	ii, 214
SELIVANOV (I. F.). Hydrates of Calcium Oxide and their Molecular Compounds	ii, 214
D'ANS (JOE) and R. SIEGLER. Solubility of the Nitrates of the Alkaline Earths in Mixtures of Alcohol and Water at 25°	ii, 214
BUNGE (CURT). Action of Aqueous Barium Hydroxide on Certain Kinds of Glass	ii, 215
WIRTH (FRITZ). The Solubility of Glucinum Sulphate in Water and Sulphuric Acid	ii, 215
ORLOV (N. A.). Glucinum Chromates	ii, 215
KALLAUNER (O.). The Thermal Dissociation of Amorphous Magnesite	ii, 215
ZOTTER (V.). Action of Hydrogen Peroxide on Alkaline Solutions of Lead Oxide	ii, 216

CONTENTS.

xiii

	PAGE
AMADORI (MARIO). Tendency to Combination between Haloids and Phosphates of the Same Metal. III. Fluoride, Chloride, and Phosphate of Lead	ii, 216
SCARPA (G.). Double Salts of Thallous Chloride with Ferric Chloride and with Bismuth Chloride	ii, 217
PADOA (MAURIZIO) and F. BOVINI [with CARLO MARANI]. Molecular Complexity in Metals in the Solid Phase	ii, 217
PUSCHIN (NIKOLAI A.) and V. N. RJASHSKI. Electrical Conductivity of Alloys of Copper and Zinc	ii, 218
LOHR (J. M.). The Tensile Strength of the Copper-Zinc Alloys	ii, 218
FOWLER (GEORGE). Some Basic Copper Sulphates	ii, 219
BANCROFT (WILDER D.) and T. R. BRIGGS. Blue Gelatin Copper	ii, 219
SCALA (ALBERTO). Action of Distilled Water on Impure Aluminium	ii, 220
CEAKO (NICOLAS). Alloys of Aluminium and Vanadium	ii, 220
WIRTH (FRITZ). The Crystallisation of Pure Aluminium Salts from Solutions containing Iron and the Artificial Preparation of Halotrichite	ii, 220
WIRTH (FRITZ). The Solubility of Aluminium and Iron Sulphates in Sulphuric Acid	ii, 221
WUNDER (L.). Ultramarine Compounds. II.	ii, 221
WEDERIND (EDGAR). The Hensler Ferromagnetic Manganese Alloys	ii, 222
CHARPY (GEORGES) and S. BONNEROT. The Reactions which Accompany the Osmosis of Hydrogen through Iron	ii, 222
HONDA (KÔTARÔ) and HIROMU TAKAGI. The Transformation of Iron and Steel at High Temperatures	ii, 222
RUFF (OTTO). The System Iron-Carbon	ii, 223
JOVITSCHITSCH (MILORAD Z.). Complete Solubility of Chromium Hydroxide in Ammonia	ii, 223
JORISSEN (ARMAND). Diffusion of Molybdenum in the Coalfield of Liège	ii, 224
ROSENHEIM (ARTHUR) and JOSUA FELIX [with JACOB PINSKER]. Iso- and Hetero-Poly-salts. VII. Molybdic Acid Hydrates and Some Polymolybdates	ii, 224
ARTMANN (PAUL). Uranyl Iodates	ii, 224
WEDERIND (EDGAR) [with HANS KUŽEL, S. JUDD LEWIS, and J. TELSTOW]. Zirconium. II.	ii, 225
MARINO (LUIGI) and R. BECARRELLI. The Subhaloid Compounds of Some Elements. I. The So-called Bismuth Subiodide	ii, 227
CORNEJO (ALFONSO). History of Colloidal Gold. I. Gold Ruby Glass	ii, 227
ROBERTS (JOSEPH H. T.). Disintegration of Metals at High Temperatures. Condensation Nuclei from Hot Wires	ii, 228

Mineralogical Chemistry.

SALOMON (WILHELM). Asphalt Veins in Quartz-Porphry near Heidelberg	ii, 229
HORN (FRANK R. VAN). [Minerals from Sierra Mojada, Coahuila, Mexico]	ii, 229
TUCAN (FRAN). The Bauxite Question	ii, 230
MANASSE (ERNESTO). Some Minerals from Tuscany	ii, 230
ROZSA (MICHAEL). The Staasfurt Deposits	ii, 231
TCHIRVINSKI (VLADIMIR). Question of the Identity of Podolite and Dabblite	ii, 231
SAMOILOV (JAKOV). Mineralogy of the [Russian] Phosphorite Deposits	ii, 231
ZEMLEY (A. E. V.). Occurrence of Scorodite in Rhodesia	ii, 232
LACROIX (ALFRED). Uranium Minerals from Prov. Itasy, Madagascar	ii, 232
MELLOR (JOSEPH W.) and A. D. HOLDCROFT. The Chemical Constitution of the Kaolinite Molecule. II.	ii, 232
HOUSTON (ROBERT S.). Mineralogy of Renfrewshire	ii, 233
MERRILL (GEORGE P.). Origin of Moldavites and Similar Sporadic Glasses	ii, 233

	PAGE
MANASSE (ERNESTO). Chloritoid (Ottrelite) from the Apuan Alps, Tuscany	ii, 234
MANASSE (ERNESTO). Composition of Some Minerals of the Chloritoid Group	ii, 234
LACROIX (ALFRED). Minerals from Ambatofotsikely, Madagascar	ii, 234
LACROIX (ALFRED). Lavas from Central Madagascar	ii, 235
MAGISTRETTI (L.) [with A. MORESCHI]. Ilmenite from the Quarries of Potstone at Sasso di Chiesa (Val Malenco)	ii, 235
BONTSCHEW (G.). Meteorite of Gumoschnik, Bulgaria	ii, 235
NASINI (RAFFAELLE) and C. PORLEZZA. Existence of Natural Ozonised Waters and Probable Theories of the Phenomenon. The "Acqua Forte" of the Bagnore of Monte Amiata	ii, 235

Analytical Chemistry.

CUMMING (ALEXANDER CHARLES). Hempel Double Pipette Modified to Facilitate Filling	ii, 236
LENZ (WILHELM). Micro-chemical Reagents	ii, 236
CHANOBL (FELIX). Apparatus for Electrolytic Estimations	ii, 236
WALBUM (L. E.). The Use of an Extract of Red Cabbage as an Indicator for the Measurement of the Hydrogen Ion Concentration	ii, 237
HUNTLY (GEORGE N.) and JOHN H. COSTE. Estimation of Moisture	ii, 237
CAMPBELL (F. H.). Estimation of Moisture in Organic Substances	ii, 238
SKERTCHLY (WILLIAM P.). Estimation of Moisture in Foods and Other Organic Substances	ii, 238
PIERARRETS (JOSEPH). Colour Reaction of Chlorates	ii, 238
SALKOWSKI (ERNST). Disturbing Influence of Alcohol on Various Reactions	ii, 238
LECLÈRE (ANDRÉ). Estimation of Hydriodic Acid in Tincture of Iodine	ii, 239
BINDER (KARL) and RUDOLF F. WEINLAND. A New and Delicate Test for Oxygen	ii, 239
MOSER (LUDWIG) and F. SEELING. Estimation of Available Oxygen in Persalts and Washing Powders with Titanium Trichloride	ii, 239
PREUSS (GEORG). Apparatus for the Estimation of Sulphur in Steel and Iron	ii, 240
CARPIAUX (EM.). A Source of Error in the Kjeldahl-Gunning Process	ii, 240
GAILLOT. Estimation of Ammoniacal Nitrogen by means of Formaldehyde	ii, 240
CANET (MAURICE). Estimation of Nitric Acid by Schloesing's Method	ii, 240
VANINO (LUDWIG) and A. SCHINNER. The Reaction between Formaldehyde and Nitrous Acid	ii, 241
KOEHLER and M. MARQUEYROL. Estimation of Nitric Oxide	ii, 241
SIMMERMAOHER (W.). Estimation of Phosphoric Acid Soluble in Citric Acid in Thomas Slag	ii, 241
GERRAVES (J. E.). Some Factors Influencing the Quantitative Estimation of Arsenic in Soils	ii, 242
LEHMANN (FRANZ). Estimation of Arsenic in Urine and Blood	ii, 242
HILPERT (SIEGFRIED) and THEODOR DIECKMANN. The Separation of Arsenic and Tungsten	ii, 242
GRÉGOIRE (ACH.), JAMES HENDRIK, EM. CARPIAUX, and E. GERMAIN. Estimation of Carbon and Carbon Dioxide	ii, 243
ANDERSON (R. P.). Portable Pettersson-Palmqvist Apparatus	ii, 243
NOLL (HERMANN). The Use of Phenolphthalein and of Rosolic Acid for the Estimation of Free Carbonic Acid in Water	ii, 243
HEBER (W.). Microchemical Reaction for Carbonates in Rock Sections	ii, 244
GIRAL PEREIRA (JOSÉ). Qualitative Organic Analysis by means of Magnesium	ii, 244
SALKOWSKI (ERNST). Detection of Silicic Acid in Urine without Incineration	ii, 244

CONTENTS.

XV

	PAGE
JEMPEL (WALTHER). Decomposition of Silicates	ii, 244
ABSTREZAT (W.). General Method for the Analysis of the Ashes of Body Fluids	ii, 244
JACHER (JULIUS F.). Evaluation of Barium Sulphide	ii, 244
ROSSHARD (EMIL) and W. BURAWZOW. Estimation of Magnesium Chloride in Water	ii, 245
HALKOWSKI (ERNST). Behaviour of Uric Acid towards Ammonia and Magnesium Salts and the Estimation of Magnesium in Urine	ii, 245
JOIST (KURT). Rapid Estimation of Zinc	ii, 245
LENHER (VICTOR) and C. O. MELOCHER. Influence of Lead on the Titration of Zinc with Ferrocyanide	ii, 245
JAMPO CERDAN (ANGEL DEL) and JOSÉ DE LA PUENTE. Colorimetric Determination of Traces of Zinc	ii, 246
WINKLER (LUDWIG W.). Detection and Colorimetric Estimation of Lead, Copper, and Zinc in Potable Water	ii, 246
PRITZ (WESLEY B), A. GUILLAUME, and JAMES R. WITHROW. Detection of Traces of Copper	ii, 247
WINDISCH (RICHARD). Estimation of Copper with Sodium Hypophosphite	ii, 247
CASILLY (EUGÈNE). Estimation of Copper in Preserved Vegetables by Means of the Spectrophotometer	ii, 247
BLONQUIST (ARVID). The Mercury Content in the Air, Dust, etc., of Places where Metallic Mercury is in Use	ii, 248
BUCHTALA (HANS). New Method for the Estimation of Mercury in Urine and in the Tissues	ii, 248
BROCKERS (WILHELM). Comparison of Farup's and Schumacher-Jung's Methods for the Estimation of Mercury in Urine	ii, 248
BARNBEEY (O. L.) and S. R. WILSON. Application of Diphenylcarbazide as Indicator in the Titration of Iron with Dichromate	ii, 248
HALKOWSKI (ERNST). Estimation of Iron in Presence of Organic Substances	ii, 248
CAMPBELL (F. H.). The Separation of Iron and Manganese	ii, 249
WUNDER (MAX) and B. JEANNERET. Analysis of Ferro-Zirconium	ii, 249
RAWLINS (HENRY J. B.). The Direct Volumetric Estimation of Tin	ii, 249
LENHER (VICTOR) and W. G. CRAWFORD. New Colorimetric Method for Titanium	ii, 250
BELLUCCI (ITALO) and L. GRASSI. Use of Cupferron in Quantitative Analysis [of Titanium]	ii, 250
REICHARD (C.). Estimation of Bismuth by Titration of the Hydrochloric Acid Solution of Bismuth Oxide by means of Alkalis	ii, 250
HARTWAGNER (FRANZ). The Reaction between Formaldehyde and Bismuth or Copper in the Presence of Strong Alkali	ii, 251
REIMBERG (E.). Estimation of Tantallic Acid and Columbic Acid in Tantalites, Columbites, Yttrotantalites, and Fergussonites, and the Colorimetric Estimation of Columbium	ii, 251
SAUL (JOHN EDWARD). Delicate Colour Reactions of Gold Salts	ii, 252
WUNDER (MAX) and V. THÜRINGER. Estimation of Palladium and its Separation from Copper and Iron	ii, 252
GRÜNHUT (LEO). A Source of Error in the Determination of "Permanganate Absorbed" by Drinking Waters by Schulze's Method	ii, 253
LEBEAU (PAUL) and A. DAMIENS. A Method of Analysing Mixtures of Hydrogen and the Gaseous Saturated Hydrocarbons, Hydrogen, Methane, Ethane, and Propane	ii, 253
HALL (S. GODFREY) and ARTHUR J. HARVEY. Estimation of Glyceryl Acetate in Essential Oils	ii, 253
JOLLES (ANOLF). Detection of Pentoses in Urines containing Dextrose	ii, 254
JÄRVINEN (K. K.). Estimation of Dextrose in Urine	ii, 254
GRIMBERT (LEON). Estimation of Reducing Sugars by Lehmann's Method	ii, 254
FAIRBERG (B. G.). Quantitative Study of Some Aldehyde Reactions	ii, 255
GAILLOT. Estimation of Formaldehyde	ii, 255
FRANKEN (WILHELM) and LEO GRÜNHUT. Detection of Citric Acid in Wine	ii, 255

	PAGE
KREIS (HANS) and EMIL ROTH. Hardened (Hydrogenised) Oils and the Detection of Arachidic Acid	ii, 256
GOLDBERG (PAUL). Estimation of Caoutchouc in Vulcanised Rubber Materials	ii, 256
VORLÄNDER (DANIEL). The Prussian Blue Reaction	ii, 257
VANIČEK (RUDOLF). Rapid Estimation of Tannin Matters and Acidity in Tanning Liquors	ii, 258
SALVATEIRA (H.). Comparative Examination of Methods for the Estimation of Dyes	ii, 259
MACADIE (W.). Chemical Detection of Veronal Poisoning	ii, 258
BAESSLER (OTTO). Rapid Estimation of Pyridine in the Presence of Ammonia in Gas Liquors	ii, 259
PUTT (EARL B.). Micro-chemical Tests for the Identification of Some of the Alkaloids	ii, 259
HARTIDGE (H.). Factors Affecting the Measurements of Absorption Bands	ii, 259
GANASSINI (DOMENICO). Behaviour of Copper Salts towards Ganassini's Reagent for Blood	ii, 260
RULLMANN (W.). Schardinger's Reaction for Cow's Milk	ii, 260
KOBER (PHILIP ADOLF). Nephelometry in the Study of Proteases and Nucleases. I.	ii, 260
GRIMMER (WALTHER). The Nature of Peroxydase	ii, 260

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS

A.

Abderhalden, E., and A. E. Lampé, i, 310.
 Abel, E., ii, 204.
 Acree, S. F. See E. K. Marshall, jun., and S. Nirdlinger.
 Agulhon, H., and R. Sazerac, i, 322.
 Allen, H. S., ii, 172.
 Alterthum, H., ii, 183.
 Amadori, M., ii, 213, 216.
 Amagat, E. H., ii, 185, 188.
 Anderson, R. P., ii, 243.
 Andre, F. See F. Reitzenstein.
 Andrae, J. L., ii, 188.
 Angelico, F., Catalano, i, 325.
 Armstrong, E. F. See F. Keeble.
 Arsenev, A. See N. S. Kurnakov.
 Artmann, P., ii, 224.

B.

Bachem, C. See H. Leo.
 Bachmann, W. See R. Zsigmondy.
 Baessler, O., ii, 259.
 Baker, R. A., ii, 205, 206.
 Bauroft, W. D., and T. R. Briggs, ii, 219.
 Barcroft, J., and J. H. Burn, i, 306.
 Barcroft, J., M. Camis, G. C. Mathison, F. Roberts, and J. H. Ryffel, i, 296.
 Barcroft, J., G. Graham, and H. L. Higgins, i, 306.
 Barcroft, J., R. A. Peters, F. Roberts, and J. H. Ryffel, i, 306.
 Barnebey, O. L., and S. R. Wilson, ii, 218.
 Barratt, J. O. W., i, 308.
 Barrio Fernández, J. See J. Muñoz del Castillo.
 Baschieri, E., ii, 213.
 Baskerville, C., and H. S. Riederer, i, 242.

Batschinski, A., ii, 188.
 Baud, E., ii, 198.
 Baudisch, O., and E. Mayer, i, 324.
 Bauer, H., i, 263.
 Beadle, C., and H. P. Stevens, i, 283.
 Beal, G. D. See W. J. Gies.
 Becarelli, R. See L. Marino.
 Becker, P. See H. Decker.
 Beckers, W., ii, 248.
 Becquersel, P., i, 322.
 Bell, J. E. See E. W. Washburn.
 Bellucci, L., and L. Grassi, ii, 250.
 Berg, W. N., i, 314.
 Berthelot, D., and H. Gaudechon, ii, 171.
 Bertrand, G., and F. Medigreceanu, i, 316.
 Bertrand, G., M. Rosenblatt, and (Mme.) M. Rosenblatt, i, 302.
 Beutner, R., i, 315.
 Bhaduri, K., i, 241.
 Bidet, F., ii, 197.
 Bieber, W., ii, 208.
 Bierling, E. See H. Schulze.
 Bierry, H., i, 303.
 Bilecki, A., ii, 205.
 Biltz, H., i, 241.
 Biltz, H., and K. Seydel, i, 297.
 Binder, K., and R. F. Weinland, ii, 239.
 Blaise, E. É., and E. Carrière, i, 248.
 Blanksma, J. J., i, 328.
 Blomquist, A., ii, 243.
 Bogdan, P., ii, 192.
 Bogojaewski, F. L., i, 301.
 Boll, M., ii, 171, 182.
 Bone, W. A., ii, 204.
 Bongrand, J. C., i, 304.
 Bonnerot, S. See G. Charpy.
 Bontschew, G., ii, 235.
 Borovikov, G. A., i, 324.
 Bosshard, E., and W. Burawzow, ii, 245.
 Boubnoff. See E. Briner.

Bougault, J., i, 269.
 Bougault, J., and Mouchel-la-Fosse, i, 247.
 Boulanger, C., and G. Urbain, ii, 203.
 Boulud, R. See R. Lépine.
 Bourquetot, E., and M. Bridel, i, 303.
 Bourquetot, E., H. Hérissé, and M. Bridel, i, 249, 323.
 Bovini, F. See M. Padoa.
 Branch, G. E. K. See A. W. Titherley.
 Brannigan, P. J., A. K. Macbeth, and A. W. Stewart, TRANS., 406.
 Braun, J. von, and E. Danziger, i, 242.
 Braun, J. von, and H. Deutsch, i, 250.
 Brett, J., T. Fassgänger, J. Houben, P. Levy, and S. Link, i, 281.
 Bridel, M. See E. Bourquetot.
 Briggs, T. R. See W. D. Bancroft.
 Brillouin, M., ii, 193.
 Briner, E., and Boubnoff, ii, 210.
 Buchtala, H., i, 318.
 Bunge, C., ii, 215.
 Burawoz, W. See E. Bosshard.
 Burge, W. E., i, 303.
 Burn, J. H., i, 306.
 Burn, J. H. See also J. Barcroft.
 Burrige, W., i, 320.
 Rutescu, D., i, 273.
 Bywaters, H. W., i, 311.

C.

Cain, J. C., ii, 169.
 Cambi, L., ii, 214.
 Camis, M. See J. Barcroft.
 Campbell, F. H., ii, 238, 249.
 Campo Cerdan, A. del, and J. de la Puente, ii, 246.
 Canet, M., ii, 240.
 Carpiaux, E., ii, 240.
 Carpiaux, E. See also A. Grégoire.
 Carré, P., i, 304.
 Carrière, E. See E. É. Blaise.
 Casali, A. See G. Scagliarini.
 Catalano, G. See F. Angelico.
 Cathcart, E. P., and H. H. Green, i, 311.
 Chablay, E., i, 241.
 Chancel, F., ii, 236.
 Chapman, D. L., and L. K. Underhill, TRANS., 496.
 Chapman, J. C., ii, 173.
 Charpy, G., and S. Bonnerot, ii, 222.
 Chattaway, F. D., ii, 209.
 Chick, (Miss) H., and C. J. Martin, i, 302.

Chejn, M., i, 282.
 Christiansen, C., ii, 177.
 Cohen, E., ii, 181.
 Collie, J. N., and H. S. Patterson, TRANS., 419.
 Comanducci, E., i, 296.
 Comte, F., ii, 210.
 Cook, F., and M. S. Pembrey, i, 305.
 Coppadoro, A., ii, 196.
 Cornejo, A., ii, 227.
 Costanzo, G., ii, 174.
 Coste, J. H. See G. N. Huntly.
 Crawford, W. G. See V. Leuther.
 Cumming, A. C., ii, 236.
 Cumming, A. C., and J. Macleod, TRANS., 513.
 Cushing, H. See L. H. Weed.
 Cusmano, G., i, 275.
 Czako, N., ii, 220.

D.

Damiens, A. See P. Lebeau.
 Danziger, E. See J. von Braun.
 Darapsky, A., i, 247.
 D'Ans, J., and R. Siegler, ii, 214.
 Datta, R. L., TRANS., 426.
 Decker, H., i, 290.
 Decker, H., and P. Becker, i, 260, 290, 291.
 Decker, H., W. Kropp, H. Hoyer, and P. Becker, i, 289.
 Decker, H., P. Becker, H. Hoyer, W. Kropp, and C. Zoellner, i, 272.
 Decker, H., and T. Eichler, i, 239.
 Denis, W. See O. Folin.
 Deutsch, H. See J. von Braun.
 Dieckmann, T. See S. Hilpert.
 Diem, L. See K. B. Lehmann.
 Duclaux, J., ii, 188.
 Dumanski, A., E. Zabolitski, and M. Evshev, ii, 194.
 Durlach, E., i, 311.

E.

Eberwein, E. See F. Russ.
 Eddy, W. H., i, 302.
 Efremov, N. N. See N. S. Kurnakov.
 Egerer, G., and H. Meyer, i, 269.
 Egger, F. See H. Franzen.
 Egidi, V. See F. C. Palazzo.
 Eibner, A., and L. Gerstaecker, i, 254.
 Eichler, T. See H. Decker.
 Enklaar, C. J., i, 242.
 Escher, H. H., i, 312.
 Evshev, M. See A. Dumanski.
 Ewins, A. J., and P. P. Laidlaw, i, 319.

F.

- Falk, K. G., and M. L. Hamlin, i, 303.
 Feinberg, B. G., ii, 255.
 Felix, J. See A. Rosenheim.
 Fichter, F., M. Jetzer, and R. Leepin, i, 279.
 Fine, M. S. See V. C. Myers.
 Fischer, H., i, 302.
 Fischer, O. See R. Meyer.
 Fischer, W. See H. Ley.
 Fischler, J., ii, 178.
 Fleck, A., TRANS., 381.
 Fleming, G. B., i, 309.
 Fürsterling, K., and V. Fréedericksz, ii, 165.
 Folin, O., and W. Denis, i, 310.
 Fosse, R., i, 327.
 Fowler, G., ii, 219.
 Francesconi, L., and E. Sernagiotto, i, 283.
 Franck, J., and G. Hertz, ii, 174.
 Frankenberg, G. See C. Schaefer.
 Franzen, H., and F. Egger, i, 322.
 Fréedericksz, V. See K. Försterling.
 Fresenius, W., and L. Grünhut, ii, 255.
 Fry, P. See O. Wallach.
 Funk, C., i, 317, 327.
 Fussgänger, T. See J. Bredt.

G.

- Gaillot, ii, 240, 255.
 Ganassini, D., ii, 260.
 Gaubert, P., i, 264.
 Gauduchon, H. See D. Berthelot.
 Geiger, G. A. See W. J. Gies.
 Germain, E. See A. Grégoire.
 Gerstacker, L. See A. Eibner.
 Gesell, R. A., i, 316.
 Gies, W. J., J. Rosenbloom, W. H. Welker, G. D. Beal, and G. A. Geiger, ii, 193.
 Gila, Pereira, J., ii, 244.
 Gjaldhæk, J. K. See V. Henriques.
 Gjdchot, M., and F. Taboury, i, 278.
 Goldberg, P., ii, 256.
 Goldschmidt, F., and L. Weissmann, ii, 178.
 Goldschmidt, G., and E. Zerner, i, 248.
 Gomburg, M., i, 257, 259.
 Gordon, M. A., i, 262.
 Graham, G. See J. Barcroft.
 Grassi, L. See I. Bellucci.
 Greaves, J. E., ii, 242.

- Greco d'Alceo, O. See A. Mazzuchelli.
 Green, A. G., and F. M. Rowe, TRANS., 508.
 Green, A. G., and S. Wolff, i, 302.
 Green, H. H. See E. P. Cathcart.
 Grégoire, A., J. Hendrick, E. Carpioux, and E. Germain, ii, 243.
 Grimbert, L., ii, 254.
 Grimmer, W., ii, 260.
 Grün, A., i, 245.
 Grünhut, L., ii, 253.
 Grünhut, L. See also W. Fresenius.
 Grünkraut, A. See G. Jantsch.
 Grunupp, H. See W. Steinkopf.
 Grund, G., i, 315.
 Gubarev, A., i, 266.
 Guillaudeu, A. See W. B. Pritz.
 Guyot, J., ii, 180.
 György, P. See P. Rona.

H.

- Hacker, C., ii, 136.
 Häussler, P. See H. Rupe.
 Hagedorn, M. See C. D. Harries.
 Hall, S. G., and A. J. Harvey, ii, 253.
 Hamlin, M. L. See K. G. Falk.
 Handovský, H., and E. P. Pick, i, 319.
 Hansen, G. H., ii, 189.
 Harries, C. D., and M. Hagedorn, i, 287.
 Harries, C. D., M. Hagedorn, W. Schönberg, and R. Seitz, i, 284.
 Hartridge, H., ii, 259.
 Hartwagner, F., ii, 251.
 Harvey, A. J. See S. G. Hall.
 Harvey, E. N., i, 312.
 Hasegawa. See K. B. Lehmann.
 Hauberrisser, E., and F. Schönfeld, i, 318.
 Hauser, O., and A. Klotz, i, 246.
 Havas, E. See F. Kehrman.
 Heeger, W., ii, 244.
 Heilbron, I. M. See F. J. Wilson.
 Hempel, W., ii, 244.
 Hendrick, J. See A. Grégoire.
 Henri, V., and R. Wurmser, ii, 171.
 Henriques, V., and J. K. Gjaldhæk, i, 302.
 Herissey, H. See E. Bourquelot.
 Hertz, G. See J. Franck.
 Heuse, W. See K. Scheel.
 Hevesy, G. von, ii, 174.
 Hevesy, G. von, and L. von Putnoký, ii, 175.
 Hewitt, J. T., and (Miss) G. R. Mann, TRANS., 324.
 Higgins, H. L. See J. Barcroft.

Hill, A. V., i, 314.
 Hilpert, S., and T. Dieckmann,
 ii, 242.
 Hirsch, P. See O. Piloty.
 Hohensiegger, C. See C. Paal.
 Holdcroft, A. D. See J. W. Mellor.
 Honda, K., and H. Takagi, ii, 222.
 Hooker, D. R., i, 305.
 Hope, E., and R. Robinson, TRANS.,
 261.
 Hopkins, F. G., and A. Neville,
 i, 312.
 Horn, F. R. Van, ii, 229.
 Houben, J. See J. Bradt.
 Houston, R. S., ii, 233.
 Howat, (Miss) I. See (Miss) I. H.
 Hyde.
 Howe, P. E., i, 312.
 Hoyer, H. See H. Decker.
 Hug, L. See W. Steinkopf.
 Hughes, A. L., ii, 172.
 Huntly, G. N., and J. H. Coste,
 ii, 237.
 Hyde, (Miss) I. H., (Miss) R. Spray,
 and (Miss) I. Howat, i, 318.

I.

Ishimori, K., i, 318.
 Ivanovski, D., i, 326.

J.

Jabłczyński, K., ii, 203.
 Jackson, C. L., and F. C. Whitmore,
 i, 273.
 Jackson, D. E., i, 319.
 Jacobson, C. See L. H. Weed.
 Jänecke, E., ii, 195.
 Järvinen, K. K., ii, 254.
 Jakubovitsch, V., i, 264.
 James, O. See C. F. Whittemore.
 Jantsch, G., and A. Grünkraut,
 i, 247.
 Jaroschy, S., i, 271.
 Javillier, M., i, 326.
 Jeanneret, B. See M. Wunder.
 Jensen, H. B., i, 328.
 Jetzer, M. See F. Fichter.
 Jolles, A., ii, 254.
 Jonas, L. See A. I. Ringer.
 Jorissen, A., ii, 224.
 Jovitschitsch, M. Z., ii, 223.
 Jungfleisch, E., ii, 205.
 Just, G., and Y. Kanko, ii, 199.

K.

Kahn, M., and J. Rosenbloom,
 i, 317.

Kallauer, O., ii, 216.
 Kardos, M. See C. Liebermann.
 Kaufmann, A., M. Kunkler, and H.
 Peyer, i, 294.
 Kaufmann, A., and L. G. Vallette,
 i, 293.
 Kauko, Y. See G. Just.
 Keeble, F., and E. F. Armstrong,
 i, 325.
 Kehrmann, F., and E. Hava,
 i, 298.
 Keiser, E. H., and L. McMaster,
 i, 245, 253.
 Klooster, H. S. van, ii, 189.
 Klotz, A. See O. Hauser.
 Kober, P. A., ii, 260.
 Koehler, and M. Marquayrol,
 ii, 241.
 Koenig, A., ii, 210.
 Körber, F., ii, 185.
 Kornfeld, F., i, 315.
 Kostytschev, S., i, 323.
 Kravec, V. See N. D. Zelinski.
 Kreis, H., and E. Roth, ii, 256.
 Kremann, R., and F. Noss, ii, 189.
 Kropp, W. See H. Decker.
 Kunkler, M. See A. Kaufmann.
 Kurnakov, N. S., S. F. Shemt-
 schushni, A. Arsenov, and V.
 Zejliger, ii, 190.
 Kurnakov, N. S., and N. N.
 Efremov, ii, 207.
 Kuzel, H. See E. Wedekind.

L.

Laar, J. J. van, ii, 193.
 Labat, A., i, 315.
 Lacroix, A., ii, 232, 234, 235.
 Laidlaw, P. P. See A. J. Ewins.
 Lampé, A. E. See E. Abderhalden.
 Langmuir, I., ii, 209.
 La Rosa, M., ii, 176.
 Lasausse, E., i, 265.
 Laub, J., ii, 177.
 Lebeau, P., and A. Damiens, ii, 253.
 Leclère, A., ii, 239.
 Leduc, A., ii, 185.
 Leepin, R. See F. Fichter.
 Lehmann, F., ii, 242.
 Lehmann, K. B., and L. Diem, i, 320.
 Lehmann, K. B., and Hasegawa,
 i, 320.
 Lemmel, L. See F. Straus.
 Lenher, V., and W. G. Crawford,
 ii, 250.
 Lenher, V., and C. C. Meloche,
 ii, 245.
 Leuz, W., ii, 236.
 Lenzinger, E. See H. Rupe.

Loe, H., i, 314.
 Leo, H., and C. Rachen, i, 314.
 Leo, H., and W. Traschennikov, i, 314.
 Lepierre, C., i, 326, 327.
 Lépine, R., and R. Boulud, i, 307.
 Levy, P. See J. Bredt.
 Lewis, S. J. See E. Wedekind.
 Ley, H., and W. Fischer, ii, 169.
 Lidholm, H., i, 252.
 Lidor, A. P., i, 252.
 Liebermann, C., i, 265.
 Liebermann, C., and M. Kardos, i, 276.
 Liebig, H. von, ii, 170.
 Lillie, R. S., i, 318.
 Link, S. See J. Bredt.
 Lippmann, E. O. von, i, 244.
 Lockemann, G., and F. Lucius, i, 296.
 Lob, W., i, 250.
 Lehr, J. M., ii, 218.
 Lucius, F. See G. Lockemann.

M.

Macadie, W., ii, 258.
 Macbeth, A. K. See P. J. Brannigan.
 McClelland, N. P. See J. E. Purvis.
 McDermott, F. A., ii, 207.
 Maclean, H., and (Miss) I. Smedley, i, 313.
 Macleod, J. See A. C. Cumming.
 McMaster, L. See E. H. Keiser.
 Magistretti, L., and A. Moreschi, ii, 235.
 Mailhe, A., i, 261.
 Mair, W. See J. L. Smith.
 Manasse, E., ii, 230, 234.
 Manevitch, B. See A. Pictet.
 Mann, (Miss) G. R. See J. T. Hewitt.
 Marani, C. See M. Padoa.
 Marchlewski, L., i, 287.
 Marino, L., and R. Bacarelli, ii, 227.
 Marogna, G. See F. C. Palazzo.
 Marquoyrol, M. See Koehler.
 Marshall, jun., E. K., S. F. Acree and C. N. Myers, i, 253.
 Martin, C. J. See (Miss) H. Chick.
 Marx, E. See W. Zaleski.
 Maryott, C. H. See R. G. Van Name.
 Mathison, G. C. See J. Barcroft.
 Matsuo, I., i, 309.
 Mauthner, F., i, 277.
 Mayer, E. See O. Baudisch.
 Mazzucchelli, A., ii, 165.
 Mazzucchelli, A., and O. Greco d'Alceo, ii, 167.
 Medigreceanu, F. See G. Bertrand.
 leimberg, E., ii, 251.

Meissner, W., ii, 185.
 Mellanby, E., i, 311.
 Mellor, J. W., and A. D. Holdcroft, ii, 232.
 Meloche, C. C. See V. Lenher.
 Meltzer, S. J., i, 320.
 Mendel, L. B. See T. B. Osborne.
 Meneghini, D., ii, 210.
 Manskutkin, B. N., i, 255, 277.
 Merrill, G. P., ii, 233.
 Mestrezat, W., ii, 244.
 Mennier, J., ii, 165.
 Meyer, H. See G. Egerer.
 Meyer, J. See N. von Peskoff.
 Meyer, K. H., ii, 204.
 Meyer, K. H., and H. Schlösser, i, 295.
 Meyer, R., and O. Fischer, ii, 167, 168.
 Michael, A., and E. Scharf, i, 246.
 Michel, F., ii, 206.
 Michiels, L., i, 244; ii, 176.
 Mie, G., ii, 192.
 Miller, J. See J. Ritchie.
 Mitchell, A. D., and C. Smith, TRANS., 489.
 Moles, E., and S. Piña de Rubies, ii, 209.
 Moreschi, A. See L. Magistretti.
 Moser, L., and F. Seeling, ii, 239.
 Moskalenko, G., i, 244.
 Mouchel-la-Fosse. See J. Bougaurl.
 Muñoz del Castillo, J., and J. Barrio Fernández, ii, 177.
 Murat, M. See P. Sabatier.
 Myers, C. N. See E. K. Marshall, jun.
 Myers, V. C., and M. S. Fine, i, 315.

N.

Name, R. G. Van, and C. H. Maryott, ii, 181.
 Nanty, T., ii, 196.
 Nasini, R., and C. Porlezza, ii, 235.
 Neville, A. See F. G. Hopkins.
 Nirdlinger, S., F. M. Rogers, and S. F. Acree, ii, 205.
 Nolan, T. J., and S. Smiles, TRANS., 340.
 Noll, H., ii, 243.
 Norris, R. V., i, 308.
 Noss, F. See R. Kremann.

O.

O'Brien, R. A., i, 308.
 Odén, S., and E. Ohlon, ii, 194.
 Östling, G. J. See W. A. Roth.
 Ohlon, E. See S. Odén.

Oppermann, F. See F. Rolly.

Orlov, A., i, 273.

Orlov, N. A., ii, 215.

Osborne, T. B., and L. B. Mendel, i, 312.

Ostwald, W., ii, 195.

P.

Paal, C., and C. Hohenegger, i, 241.
Padoa, M., F. Bovini, and C. Marani, ii, 217.

Palazzo, F. C., i, 253.

Palazzo, F. C., and V. Egidi, i, 249.

Palazzo, F. C., and G. Marogna, i, 300.

Pascal, P., ii, 182.

Patein, G., i, 316.

Patterson, H. S. See J. N. Collie.

Pembrey, M. S. See F. Cook.

Peskoff, N. von, and J. Meyer, ii, 201.

Peters, R. A. See J. Barcroft.

Peyer, H. See A. Kaufmann.

Pick, E. F. See H. Handovsky.

Pictet, A., and B. Manevitch, i, 295.

Pieraerts, J., ii, 233.

Piest, C., i, 250.

Pilcher, J. D., i, 317.

Piloty, O., and P. Hirsch, i, 292.

Pina de Rubies, S. See E. Moles.

Pinsker, J. See A. Rosenheim.

Plimmer, R. H. A., i, 302, 310.

Plotnikov, V. A., ii, 179.

Pope, W. J., i, 305.

Pope, W. J., and J. Read, TRANS., 444.

Porlezza, C. See R. Nasini.

Power, F. B., and A. H. Salway, TRANS., 399.

Prandtl, W., ii, 206.

Preuss, G., ii, 240.

Pritz, W. B., A. Guillaudeu, and J. R. Withrow, ii, 247.

Puente, J. dela. See A. del Campo Cerdan.

Purvis, J. E., and N. P. McClelland, TRANS., 433.

Puschin, N. A., and V. N. Rjashski, ii, 218.

Putnoky, L. von. See G. von Hevesy.

Putt, E. B., ii, 259.

Q.

QuagliarIELLO, G., i, 320.

R.

Rawlins, H. J. B., ii, 249.

Read, J. See W. J. Pope.

Reed, W. W., ii, 186.

Reichard, C., ii, 250.

Reitzenstein, F., and F. Andre, i, 200.

Reynolds, J. E., ii, 212.

Rhead, T. F. E., and R. V. Wheeler, TRANS., 461.

Richardz, F., ii, 184.

Richter, O., ii, 184.

Riederer, H. S. See C. Baskerville.

Riiber, C. N., i, 274.

Ringer, A. L., and L. Jones, i, 319.

Ritchie, J., and J. Miller, i, 308.

Rivett, A. C. D., ii, 202.

Rjashski, V. N. See N. A. Puschin.

Roberts, F. See J. Barcroft.

Roberts, J. H. T., ii, 228.

Robin, A., i, 317.

Robinson, R. See E. Hope.

Rogers, F. M. See S. Nirdlinger.

Rohde, G. See G. Schultz.

Rolly, F., and F. Oppermann, i, 307.

Romanov, W., ii, 182.

Róna, E., ii, 199.

Rona, P., and P. György, i, 308.

Rosanoff, M. A., ii, 204.

Rose, A. R., i, 249.

Rosenblatt, M. See G. Bertrand.

Rosenblatt, (Mme.) M. See G. Bertrand.

Rosenbloom, J., i, 312.

Rosenbloom, J., and W. Weinberger, i, 319.

Rosenbloom, J. See also W. J. Gies and M. Kahn.

Rosenheim, A., J. Felix, and J. Pinsker, ii, 224.

Ross, P. A., ii, 145.

Rossi, P., ii, 175.

Roth, E. See H. Kreis.

Roth, W. A., and G. J. Ostling, ii, 187.

Rowe, F. M. See A. G. Green.

Rózsa, M., ii, 231.

Ruff, O., ii, 223.

Rullmann, W., ii, 260.

Kupe, H., P. Häussler, E. Leuzinger, and G. Wolfsleben, i, 266.

Rupe, H., and G. Wolfsleben, i, 264.

Russ, F., and E. Eberwein, ii, 186.

Ryffel, J. H. See J. Barcroft.

S.

- Sabatier, P., and M. Murat, i, 255.
 Sacher, J. F., ii, 244.
 Salkowski, E., i, 322; ii, 238, 244, 245, 248.
 Salomon, W., ii, 229.
 Salvaterra, H., ii, 258.
 Salway, A. H., TRANS., 351.
 Salway, A. H., See also F. B. Power.
 Samoilov, J., ii, 281.
 Saul, J. E., ii, 252.
 Sazerac, R. See H. Agulhon.
 Sborgi, U., ii, 213.
 Scagliarini, G., and A. Casali, ii, 181.
 Scala, A., ii, 220.
 Scarpa, G., ii, 217.
 Schaefer, C., and G. Frankenberg, ii, 191.
 Schaposchnikov, V. G., i, 301.
 Scharf, E. See A. Michael.
 Scheel, K., and W. Heuse, ii, 183.
 Schiener, A. See L. Vanino.
 Schlösser, H. See K. H. Meyer.
 Schmidt, F., ii, 190.
 Schmidt, H., ii, 211.
 Schönberg, W. See C. D. Harries.
 Schönfeld, F. See E. Hauberrisser.
 Schreinemakers, F. A. H., ii, 196.
 Schtscherbak, B. See N. D. Zelinski.
 Schtscherica, E., i, 244.
 Schultz, G., and G. Rohde, i, 296.
 Schultze, G., ii, 192.
 Schulze, H., and E. Bierling, i, 237.
 Schvecof, B., ii, 193.
 Schwarz, H., ii, 189.
 Seeling, F. See L. Moser.
 Seitz, R. See C. D. Harries.
 Selivanov, F., ii, 214.
 Sernagiotto, E. See L. Francesconi.
 Seydel, K. See H. Biltz.
 Shedden, F., ii, 208.
 Shemtschushni, S. F. See N. S. Kurnakov.
 Siegler, R. See J. D'Ans.
 Simmermacher, W., ii, 241.
 Skertchly, W. P., ii, 238.
 Smedley, (Miss) I. See H. Maclean.
 Smiles, S. See T. J. Nolan.
 Smith, C. See A. D. Mitchell.
 Smith, J. L., and W. Mair, i, 313.
 Spray, (Miss) R. See (Miss) I. H. Hyde.
 Stark, J., ii, 166, 172.
 Steche, O. See P. Waentig.
 Steinkopf, W., H. Grünupp, and L. Hug, i, 246.
 Steubing, W., ii, 166.

- Stevens, H. P. See C. Beadla.
 Stewart, A. W. See P. J. Branigan.
 Stoklasa, J., i, 324.
 Straus, F., and L. Lemmel, i, 256.
 Strube, V. See D. Vorländer.

T.

- Taboury, F. See M. Godchot.
 Takagi, H. See K. Honda.
 Tammann, G., ii, 193.
 Tashiro, S., i, 313.
 Tassilly, E., ii, 247.
 Tauchert, F., ii, 211.
 Teletow, J. See E. Wedekind.
 Thiel, A., ii, 199.
 Thole, F. B., TRANS., 317.
 Thomas, C., i, 320, 327.
 Thüringer, V. See M. Wunder.
 Tiede, E., ii, 210.
 Titherley, A. W., and G. E. K. Branch, TRANS., 330.
 Traschnonnikov, W. See H. Leo.
 Tschelincev, V. V., i, 245, 251.
 Tschirvinski, V., ii, 231.
 Tücan, F., ii, 230.

U.

- Underhill, L. K. See D. L. Chapman.
 Urbain, G. See C. Boulanger.

V.

- Vallette, L. G. See A. Kaufman.
 Vaniček, R., ii, 258.
 Vanino, L., and A. Schinner, ii, 207, 241.
 Voigt, K., ii, 245.
 Vorländer, D., ii, 257.
 Vorländer, D., and W. Strube, ii, 198.

W.

- Waentig, P., and O. Steche, i, 304.
 Wagner, C. L., ii, 200.
 Wahl, W., ii, 208.
 Walbum, L. E., ii, 237.
 Wallach, O., and P. Fry, i, 278.
 Washburn, E. W., and J. E. Bell, ii, 177.

- Weber, S., i, 301.
 Wedekind, E., ii, 222.
 Wedekind, E., H. Kužel, S. J. Lewis, and J. Teletow, ii, 225.
 Weed, L. H., H. Cushing, and C. Jacobson, i, 309.
 Wegrzynowski, L., i, 313.
 Weinberger, W. See J. Rosenbloom.
 Weinland, R. F. See K. Binder.
 Weissmann, L. See F. Goldschmidt.
 Weitzenböck, R., i, 259.
 Welker, W. H. See W. J. Gies.
 Wheeler, R. V. See T. F. E. Rhead.
 Whipple, G. H., i, 317.
 Whitmore, F. C. See C. L. Jackson.
 Whittemore, C. F., and C. James, i, 248.
 Wichelhaus, H., i, 261.
 Willberg, M. A., i, 321.
 Wilsar, H., ii, 172.
 Wilson, F. J., and I. M. Heilbron, TRANS., 377.
 Wilson, S. R. See O. L. Barnebey.
 Windisch, R., ii, 247.
 Winkler, L. W., ii, 246.
 Wirth, F., ii, 215, 220, 221.
 Withrow, J. R. See W. B. Pritz.
 Wolff, P., i, 304.
 Wolff, S. See A. G. Green.
 Wolfleben, G. See H. Rupe.
 Wunder, L., ii, 221.
 Wunder, M., and B. Jeanneret, ii, 249.
 Wunder, M., and V. Thüringer, ii, 252.
 Wurmser, R. See V. Henri.

Z.

- Zabotinski, E. See A. Dumanski.
 Zaleski, W., and E. Marx, i, 325.
 Zampolli, L. M., i, 296.
 Zealley, A. E. V., ii, 282.
 Zejliger, V. See N. S. Kurnakov.
 Zelinski, N. D., V. Kravec, and B. Schtscherbak, i, 255.
 Zerner, E. See G. Goldschmidt.
 Zipfel, H., i, 323.
 Zoellner, O. See H. Decker.
 Zotier, V., ii, 216.
 Zsigmondy, R., and W. Bachmann, ii, 194.

ERRATA.

VOL C (ABSTR., 1911).

Page.	Line.	
i, 870	14	<i>delete</i> "m. p. 65."

VOL. CIII (TRANS., 1913).

153	27	<i>for</i> "ethyl di- <i>p</i> -toluoyl." <i>read</i> "ethyl di- <i>p</i> -nitrobenzoyl."
165	1	asterisk refers to footnote on p. 164.

VOL. CIV (ABSTR., 1913).

i, 177	8	<i>for</i> "benzoate (n_D^{20} 1.5071)" <i>read</i> "cyclohexanecarboxylate."
i, 177	9	"cyclohexanecarboxylate", "benzoate (n_D^{20} 1.5071)."

In the same region the Ostwald law for "weak" electrolytes reduces to

$$(1 - \alpha) = k^{-1} \times \text{Constant.}$$

Here the mass relation appears in its simplest terms, since in both cases progressive hydration has proceeded so far that molecular varieties have been reduced to the fewest. These two simple formulæ thus bring out the fundamental difference between the class of "weak" electrolytes of which acetic acid is an example, and the class of "strong" electrolytes, of which potassium chloride is an example.

For weak electrolytes the active mass of the undissociated fraction at great dilution is inversely proportional to the mass of the water.

For strong electrolytes the active mass of the undissociated fraction at great dilution is inversely proportional to the square root of the mass of the water.

Here, where the problem is simplest, is the point where reconciliation with the law of mass action as usually enunciated must begin. It is proposed to consider this aspect of the matter in a subsequent paper.

ST. SWITHINS,
HENDON, N.W.

XXXIX. — *Viscosity and Association. Part IV. The Viscosity of the Aromatic Amines.*

By FERDINAND BERNARD THOLE.

THE mutual effect of different unsaturated nuclei in a molecule has been studied from many points of view and by many different methods, both chemical (compare V. Meyer, Sudborough, and their co-workers, and Clarke) and physical. The main drawback attached to the former method lies in the undoubtedly very complex and sensitive nature of the inter-atomic forces which are greatly influenced, even by the addition of a comparatively inert solvent, and necessarily to a much greater degree by chemically active reagents.

Some time ago (T., 1910, 97, 2596) the author investigated by the viscometric method the influence of various substituents in various spatial positions on the degree of association of phenol.

The results agreed closely with those derived from other physical properties, and showed that ortho-substitution has the greatest, and para-substitution the least, influence on the associating tendency of the hydroxyl group.

More important, however, is the nature of the substituent groups. Those which exhibit a considerable degree of unsaturation have the greatest effect in repressing association presumably by "binding" some of the residual affinity of the hydroxyl group. It was found possible, in fact, to arrange in series a number of common radicles in order of their inhibiting influence on phenolic association, and this order exactly paralleled with that obtained by arranging the same groups in order of their influence on molecular magnetic rotation. The most active of these were the carbethoxyl, aldehyde, and nitro-radicles, and the least active the chlorine and methyl radicles.

Investigation of solutions of the phenols in various solvents, both "dissociating" and "non-dissociating," showed the great extent of aggregate-disruption that was produced even by solvents of the latter class.

In the present paper a number of aromatic amines have been investigated with a view to ascertain whether the amino-group (which, like the hydroxyl group, possesses considerable residual affinity) is affected in the same way by substituent groups of varying residual affinity in varying positions in the benzene nucleus. This work also appeared of considerable interest, since a recent investigation on the viscosity of the amines (Mussell, Thole, and Dunstan, T., 1912, 101, 1008), although carried out from a somewhat different point of view, directed attention to certain molecular influences which exert a very notable effect on viscosity. By comparing the values of $\frac{\eta}{\text{Mol. vol.}} \times 10^3$ it was shown

that as a general rule secondary amines are less viscous than primary amines, whilst tertiary amines are still less viscous, that is, the substitution of amino-hydrogen atoms by alkyl groups depresses viscosity, owing either to some specific property of the hydrogen atom or to the increasing symmetry of the molecule. When, however, these hydrogen atoms are replaced by groups containing centres of unsaturation, such as the acetyl, phenyl, benzyl, and to a less degree the allyl residues, the viscosity of the amine is enhanced instead of being diminished. This new influence, which overwhelms or at least profoundly modifies the other factors involved, was termed "reinforced conjugation."

Certain anomalies which have been observed in other series of compounds, both aromatic and aliphatic, have also been shown to be due to the existence of this molecular condition (Dunstan, Hilditch, and Thole, this vol., p. 133).

EXPERIMENTAL.

The apparatus used in this work was of the new pattern recently described by the author (this vol., p. 22), and the experimental methods were similar to those detailed in previous communications.

The materials used were partly purchased and partly prepared by well known methods. In each case they were carefully purified before use.

Whenever possible the amines were investigated in the fused condition, but as many are solid at temperatures below 100° it proved necessary to compare their viscosities in some comparatively neutral solvent. The liquid chosen was amyl acetate, which has proved a valuable solvent in previous work in this connexion in view of its comparatively small dissociating tendencies and its excellent solvent powers. It will, however, be noticed that even amyl acetate produces a considerable effect on the molecular condition of the solute.

The solutions used were of equimolecular strength, and were prepared by weighing 0.005 gram-molecule of the amine in a stoppered weighing bottle, and dissolving in 7 c.c. of amyl acetate a concentration usually equivalent to about 12 per cent. In a few cases where such concentrated solutions could not be prepared, a solution of one-half this concentration was investigated, and the equivalent values for the stronger solution obtained by extrapolation.

The viscosities of the fused amines were determined at 55° and those of the solutions at 25° , the temperatures of the thermostats being controlled between very narrow limits ($\pm 0.05^{\circ}$ and $\pm 0.01^{\circ}$ respectively) by sensitive toluene regulators.

The viscosity values for the pure amines have been compared by use of the expression $\frac{\eta}{\text{Mol. vol.}} \times 10^6$. The use of this quantity for comparison purposes is undoubtedly open to several objections, but previous work has shown that it offers the most suitable method at present available for comparing the viscosities of liquids, particularly where these are of similar chemical nature.

The results for the solutions have been compared by calculating the increase produced in the product viscosity \times density $\times 10^6$ of the pure solvent per unit of molecular weight of the dissolved amine. This quantity is termed Δ in the table of results.

TABLE I.—Pure Amines at 55°.

Amine.	Density 55°/4°	Viscosity.	$\frac{\eta}{\text{Mol. vol.}} \times 10^6$.
Aniline	0.9913	0.01709	182
<i>o</i> -Chloroaniline	1.182	0.01647	153
<i>m</i> -Chloroaniline	1.184	0.01764	164
<i>p</i> -Chloroaniline	1.178	0.01964	182
<i>o</i> -Toluidine	0.9700	0.01711	155
<i>m</i> -Toluidine	0.9603	0.01513	136
<i>p</i> -Toluidine	0.9593	0.01557	140
<i>o</i> -Anisidine	1.064	0.02211	191
<i>p</i> -Anisidine	1.092	0.03215	286
Ethyl anthranilate	1.088	0.03258	215
Methylaniline	0.9571	0.01084	96.9
Ethylaniline	0.9319	0.01081	83.3
<i>iso</i> -Amylaniline	0.8912	0.01724	94.3
Allylaniline	0.9536	0.01414	101
Diphenylamine	0.9633	0.04660	266
Benzylaniline	1.038	0.05388	306
Benzylideneaniline	1.038	0.03985	229
Methyl- <i>o</i> -toluidine	0.9500	0.01171	92.0
Methyl- <i>p</i> -toluidine	0.9348	0.01220	94.2
Ethyl- <i>o</i> -toluidine	0.9220	0.01100	75.1
Ethyl- <i>p</i> -toluidine	0.9148	0.01211	82.1
Dimethylaniline	0.9274	0.00844	64.7
Methylethylaniline	0.9193	0.00972	66.2
Diethylaniline	0.9196	0.01102	68.0
Diisocamylaniline	0.8668	0.02923	109
Methylallylaniline	0.9242	0.01068	67.1
Benzylethylaniline	1.001	0.04772	226
Dimethyl- <i>o</i> -toluidine	0.9063	0.00881	58.7
Dimethyl- <i>p</i> -toluidine	0.9116	0.00864	58.3
Dimethyl- α -naphthylamine	1.013	0.03248	192
Dimethyl- β -naphthylamine	1.026	0.03365	202

TABLE II.—Solutions at 25°.

Amine.	Density 25°/4°.	Viscosity.	Δ .
Aniline	0.8778	0.008845	9.0
<i>o</i> -Chloroaniline	0.8940	0.009250	10.5
<i>m</i> -Chloroaniline	0.8945	0.009621	12.5
<i>p</i> -Chloroaniline	0.8949	0.009591	13.0
2:4-Dichloroaniline	0.9088	0.009788	12.9
2:4:6-Trichloroaniline	0.9229	0.009851	11.0
<i>o</i> -Bromoaniline	0.9161	0.009663	11.5
<i>p</i> -Bromoaniline	0.9199	0.009845	12.7
2:4-Dibromoaniline	0.9603	0.01041	12.2
2:6-Dibromoaniline	0.9760	0.00997	11.2
2:4:6-Tribromoaniline	1.002	0.01017	9.9
<i>p</i> -Iodoaniline	0.9530	0.01011	12.4
2:4-Di-iodoaniline	1.021	0.01120	13.1
<i>o</i> -Anisidine	0.8842	0.009215	10.0
<i>o</i> -Toluidine	0.8771	0.008841	7.7
<i>m</i> -Toluidine	0.8763	0.008816	7.4
<i>p</i> -Toluidine	0.8763	0.008816	7.4
Ethyl anthranilate	0.8918	0.00992	11.6
Ethyl <i>p</i> -aminobenzoate	0.8943	0.01130	10.2
<i>o</i> -Phenylenediamine	0.8842	0.009834	10.3
<i>m</i> -Phenylenediamine	0.8868	0.01009	13.7
<i>o</i> -Nitroaniline	0.9015	0.01012	15.9
<i>m</i> -Nitroaniline	0.9011	0.01041	17.3
α -Naphthylamine	0.8893	0.01031	15.7
β -Naphthylamine	0.8898	0.01030	15.6
Diphenylamine	0.8944	0.01071	22.4

Discussion of Results.

Table I.—The values obtained for the liquid amines bear out the results obtained in the previous communication on these substances. Moreover, the greater number and range of amines investigated afford new evidence as to the influence on the molecule of substitution in the amino-group and in the benzene nucleus.

Dealing first with the former type of substitution it is seen that as a general rule primary amines have a high viscosity, the secondary amines being less viscous and the tertiary still less so. In the two latter classes it will be noticed that the viscosity factor increases slowly with increasing molecular weight of the alkyl groups, although it still remains much smaller than the average value for a primary amine. The first member of the series, methyl-aniline, appears to be slightly anomalous, the viscosity being distinctly higher than that of ethylaniline.

When the amino-hydrogen atoms are replaced by groups possessing considerable residual affinity the above general rule is reversed, and the difference is most marked when the substituent group contains a phenyl nucleus; thus benzylaniline, diphenylamine, and benzylideneaniline are much more viscous even than aniline, whilst the viscosity of allylaniline, although of the same order of magnitude as the simple secondary amines, shows a quite evident exaltation due to the unsaturated character of the allyl grouping. In the case of the tertiary amines the powerful influence of the benzyl nucleus (for example, in benzylethylaniline) is still apparent, but in methylallylaniline the allyl group exerts but little exalting effect.

Since it is well known that increase in symmetry tends to diminish viscosity, it is evident that the exaltation produced by the introduction into the amino-group of unsaturated residues is due to what may be termed conjugated residual affinity. Its effect is shown much more markedly in this series of compounds than in any others hitherto examined, probably because three notably unsaturated nuclei are concerned.

Many other instances of this phenomenon may be cited, for example, the high viscosity of acetanilide as compared with that of aniline.

Owing to the inconveniently high melting points of many aniline derivatives, the influence of ortho-meta-para-substitution has not been studied very fully with the pure fused amines. It will be noticed, however, that as a general rule the ortho-compound has the lowest and the para the highest viscosity of the three isomerides,

a condition which is in exact agreement with that found in the case of the phenols. The nature of the substituent group also has an important effect, alkyl and chlorine substituents depressing the viscosity of the parent amine, whilst carbethoxyl and methoxyl augment it.

Table II.—The very great alteration produced in the condition of the molecules of a solute by the addition of a solvent is most strikingly shown by the results obtained with the amyl acetate solutions. It will be noticed that the order of viscosities is in general considerably different from that followed by the pure amines, and only the more strongly marked characteristics of the latter persist in solution.

Moreover, the relative effects of conjugation in the benzene nucleus by *o*-, *m*-, and *p*-substituents, conjugation in the amino-nucleus, and symmetry are profoundly modified, the effect of the first being emphasised and of the last minimised by solution.

Considering the results in fuller detail it will be noticed that the least viscosity increment is produced by the toluidines. The depressing effect of the substituent methyl group has already been pointed out in connexion with the results in table I.

A further striking point is the comparatively great reduction produced in the viscosity of aniline and the toluidines by solution.

The progressive substitution of the benzene ring by halogens produces particularly interesting results. Considering first the chlorine derivatives, it will be observed that the viscosity of aniline is augmented by chlorination, the ortho-substituent having the least and the para the greatest effect. Further substitution, however, depresses the viscosity increment slightly in 2:4-dichloroaniline and to a considerably greater degree in trichloroaniline.

In the bromo-derivatives a similar but more marked effect is evident, tribromoaniline having a particularly low viscosity. Moreover, the viscosity of 2:6-dibromoaniline is considerably less than that of the 2:4-isomeride, where the bromine atoms are less intimately associated with the amino-group.

p-Iodoaniline has a still lower viscosity than the chloro- or bromo-compounds, but in 2:4-di-iodoaniline the viscosity rises again, probably owing to the highly unsymmetrical loading of the benzene ring.

Whereas the alkyl and methoxyl groups and the halogen atoms have a depressing or very slightly elevating action on the viscosity of the parent amine substitution of the carbethoxyl, nitro- and amino-complexes in the benzene nucleus has a most marked effect in raising the viscosity, the value of the increment rising to about 19. With the phenylenediamines and nitroanilines this figure is

almost reached by the meta-compounds, and from analogy to the other series examined the para-compound would give a value even in excess of this. Unfortunately, experimental verification was prevented by the sparing solubility of the substances in question.

The same effect, although to a more modified degree, is shown in the naphthylamines, where a fused benzene ring takes the place of a simple substituent.

It is noteworthy that the nitro- and carbethoxyl groups which enhance so considerably the viscosity increment in this series are also the most active in repressing the association of phenol, and, further, together with the amino-group, produce very marked anomalies in the molecular refractivity of their benzenoid derivatives.

A still further point of interest lies in the fact that the difference between the viscosity of ortho- and para-isomerides is greatest in the case of the aminobenzoic esters and nitroanilines, and least with the alkyl and halogen derivatives.

Apart from these few parallels, however, there is little resemblance between the behaviour of phenols and amines when substituted by different groups. In the former compounds apparently the only variable condition which affects the viscosity to any notable extent is the degree of association, and this is almost exclusively connected with the position and degree of residual affinity of the substituting group. Moreover, the action of the solvent was merely to decrease greatly the association without producing any alteration in the order of the degree of influence of the groups.

In the amines, on the other hand, one has the effect of the conflicting variables of association, conjugation in the amino-group and in various positions in the benzene nucleus, and symmetry brought out in a very marked manner. Moreover, these influences are considerably affected and to very different extents by the influence of the solvent.

So complex, in fact, is the net result of the various factors which influence the viscosity of these compounds that it is desirable at present not to do more than direct attention to the general regularities that are apparent, without pressing too far speculations on the resultant effect of such a complex system of intramolecular and intermolecular forces.

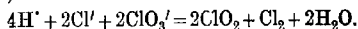
The author desires to express his indebtedness to the Research Fund Committee of the Chemical Society for a grant which has partly covered the expenses of the research.

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XL.—The Reaction between Ferric Salts and Thiosulphates.

By JOHN THEODORE HEWITT and GLADYS RUBY MANN.

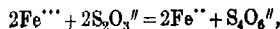
AMONGST the comparatively few quadrimolecular reactions which have been studied, reference may be made to the reduction of chromic acid by phosphorous acid (G. Viard, *Compt. rend.*, 1897, 124, 148), the interaction of hydrobromic and bromic acids (W. Judson and J. W. Walker, T., 1898, 73, 410), the bromination of benzene (L. Bruner, *Zeitsch. physikal. Chem.*, 1902, 41, 513), and the decomposition of potassium chlorate at 395° (J. Scobai, *Zeitsch. physikal. Chem.*, 1903, 44, 319). Of these reactions the first and second appear to be fairly straightforward, although it should be noted that the decomposition of hydrochloric and chloric acids appears to be of the eighth order, which is to be explained on the assumption that the reaction depends on the ions of the respective acids (R. Luther and F. H. MacDougall, *Zeitsch. physikal. Chem.*, 1908, 62, 199):



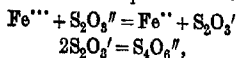
The bromination of benzene and the decomposition of potassium chlorate are attended by side-reactions, so that an addition to the known number of quadrimolecular reactions appears desirable.

Our attention was called to the reaction between ferric salts and sodium thiosulphate in working out a method for estimating the relative amounts of ferrous and ferric iron present in a solution containing considerable quantities of organic matter (*Analyst*, 1912, 37, 179). The presence of organic matter precluded the use of permanganate or dichromate for oxidation of the ferrous iron; reduction of the ferric iron with stannous or titanous chlorides was equally undesirable on account of the well-known behaviour of these reagents towards easily reducible organic substances. The use of sodium thiosulphate as a reducing agent for the ferric salts offered a possible solution of the difficulty, and eventually satisfactory results were obtained in so far as the estimation of the iron in the two states of oxidation was concerned. At the same time our attention was drawn to the slowness of the reaction between certain ferric compounds and thiosulphates, so that we considered it advisable to measure the rate of reaction and determine the velocity constants in certain cases.

A ferric salt on reduction with a thiosulphate ought to behave as if the reaction were of the fourth order in accordance with the equation:

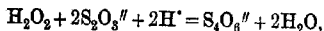


although the possibility of an apparently bimolecular reaction is not excluded if the reaction takes place in two successive stages:



the second stage being more rapid than the first.

Anomalies are occasionally found in reduction by thiosulphates; thus the reaction between hydrogen peroxide and thiosulphates in acid solution:



is apparently bimolecular; as an explanation the separation of electrically neutral S_2O_8 has been given (Emil Abel, *Monatsh.*, 1907, 28, 1239).

Whilst the reduction of salts like ferric chloride is too rapid for determination of the velocity of the reaction, ferric alum and solutions containing thiocyanates, phenol, etc., were found to be measurable; the reactions were always of the fourth order, and consequently one may conclude that it is necessary that four molecules or ions react simultaneously and the transient existence of ions, $\text{S}_2\text{O}_8'$, is excluded. The constancy of the "constants" determined leaves much to be desired, but when it is borne in mind that the reaction between $N/80$ -solutions of iron (as ferric alum) and sodium thiosulphate is half completed in about eleven minutes at 0° , it will be seen that the experimental work is not of the easiest; whilst the choice of 0° instead of 25° for carrying out the reaction, and the abandonment of attempts to measure the velocities of the reactions between sodium thiosulphate and ferric chloride or of ferric solutions to which only 3 molecules of potassium thiocyanate had been added per atom of iron, will occasion no surprise. The velocities actually determined were those of the reactions between $N/80$ -sodium thiosulphate and $N/80$ -ferric alum alone or with addition of 4 or 12 molecules of potassium thiocyanate, 4 molecules of phenol, or 4 molecules of ethyl acetoacetate. In all these cases there was no doubt that the reaction was of the fourth order; calculation showed that any other order of reaction was excluded.

EXPERIMENTAL.

Stock solutions were made of ammonia iron alum and sodium thiosulphate. The former contained 2.7925 grams of iron per litre, and was made by weighing out an exact amount of the alum in which the iron had been gravimetrically estimated. (Found, 11.65 and 11.62. Theory, 11.58.) The sodium thiosulphate was $N/40$ (6.2055 grams per litre). In carrying out a measurement, all solutions were cooled to 0° , 25 c.c. of the iron solution were trans-

ferred to a flask previously cooled, 25 c.c. of water or of a solution of thiocyanate, phenol, etc., added; then 50 c.c. of the thiosulphate solution, and the time noted. Samples of 10 c.c. were withdrawn at intervals of about 2 minutes, and transferred to flasks containing excess of solution of disodium phosphate and sodium acetate; both ferrous and ferric salts were thus precipitated, and further reaction of the ferric salt with the thiosulphate prevented. After addition of starch the remaining thiosulphate was titrated with $N/80$ -iodine; the number of c.c. used, subtracted from 10, gave the number of c.c. of thiosulphate which had already reacted with the ferric solution. No inconvenience was caused by the presence of the phosphates of iron. The units employed in calculating the reaction constants from the formula for a quadrimolecular reaction:

$$k = \frac{1}{t} \frac{1}{3} \left\{ \frac{1}{(a-x)^3} - \frac{1}{a^3} \right\}$$

are arbitrary. $a=10$ (that is, the number of c.c. of reacting mixture withdrawn for each titration); $a-x$ is then given directly by the number of c.c. of iodine used in titrating the unused thiosulphate. The constants recorded must be multiplied by 80³ if the results are desired for normal solutions (1 c.c. being still the unit of volume).

(i) *Ferric Alum and Thiosulphate.*

25 C.c. $N/20$ -ferric alum solution, 25 c.c. distilled water,
50 c.c. $N/40$ -sodium thiosulphate.

$$t = \text{seconds, } a = 10, k = \frac{1}{t} \frac{1}{3} \left\{ \frac{1}{(a-x)^3} - \frac{1}{a^3} \right\}.$$

I.			II.		
t .	$a-x$.	k .	t .	$a-x$.	k .
133	7.69	0.3007×10^{-5}	113	7.95	0.2920×10^{-5}
279	6.50	0.3156	248	5.78	0.2970
402	5.82	0.3375	374	5.93	0.3382
529	5.58	0.2997	516	5.40	0.3457
646	5.02	0.3563	663	5.00	0.3511
804	4.69	0.3603	819	4.69	0.3539
954	4.39	0.2785	1017	4.23	0.4005
1078	4.14	0.4047	1128	4.18	0.3646
1257	3.95	0.4039			
Mean.....		0.3365×10^{-5}	Mean.....		0.3419×10^{-5}

Mean of both series, 0.3392×10^{-5} .

(ii) *Ferric Alum, Potassium Thiocyanate, and Thiosulphate.*

In the first experiments made on the rate of reaction of solutions of ferric thiocyanate (iron alum and potassium thiocyanate), an

attempt was made to follow the course of the reaction colorimetrically. Although the results obtained furnished no useful constants, it was found that whilst the reaction proceeded rapidly when only three molecular proportions of potassium thiocyanate were added per atom of ferric iron, the rate of reduction by sodium thiocyanate was greatly reduced when the potassium thiocyanate was added in considerable excess to the ferric solution. The results obtained with 4 and 12 molecules of potassium thiocyanate per atom of iron are recorded.

(iia) $1\text{Fe} : 4\text{KCNS} : 1\text{Na}_2\text{S}_2\text{O}_3$.

25 C.c. $N/20$ -ferric alum, 25 c.c. $4N/20$ -KCNS,
50 c.c. $N/40$ -sodium thiosulphate.

t	$a-x$	k	t	$a-x$	k	t	$a-x$	k
129	4.66	2.295×10^{-5}	129	4.55	2.485×10^{-5}	144	4.45	2.395×10^{-5}
249	3.65	2.620	265	3.60	2.571	289	3.45	2.693
374	3.05	3.055	402	3.09	2.727	483	2.91	2.731
504	2.98	2.232	534	2.81	2.812	659	2.67	2.608
613	2.67	2.802	649	2.60	2.871	858	2.46	2.572
760	2.43	3.012	783	2.49	2.715	1008	2.26	2.839
907	2.31	2.945	929	2.32	2.837	1174	2.19	2.673
1095	2.19	2.868	1098	2.19	2.860	1388	1.99	3.021
1220	2.19	2.574	1224	2.11	2.938	1550	1.93	2.969
Mean...		2.712×10^{-5}	Mean...		2.757×10^{-5}	Mean ..		2.722×10^{-5}

Mean of three series, 2.730×10^{-5} .

It will be seen that the reaction is half completed in about two minutes, and great constancy of k is not to be expected.

(iib) $1\text{Fe} : 12\text{KCNS} : 1\text{Na}_2\text{S}_2\text{O}_3$.

25 C.c. $N/20$ -ferric alum, 25 c.c. $12N/20$ -KCNS,
50 c.c. $N/40$ -sodium thiosulphate.

t	$a-x$	k	t	$a-x$	k
109	7.40	0.4492×10^{-5}	268	6.05	0.4438×10^{-5}
282	6.09	0.4262	451	5.35	0.3993
391	5.50	0.3331	563	4.91	0.4211
494	5.22	0.4069	698	4.69	0.4151
613	4.91	0.4056	809	4.42	0.4343
733	4.64	0.3836	958	4.28	0.4092
1019	4.33	0.3707	1090	4.09	0.4165
1124	4.09	0.3622	1225	3.96	0.4110
1270	3.92	0.4096			
Mean.....		0.3945×10^{-5}	Mean.....		0.4188×10^{-5}

Mean of both series, 0.4066×10^{-5} .

(iii) *Ferric Alum, Phenol, and Sodium Thiosulphate.*

25 C.c. *N*/20-ferric alum, 25 c.c. 4*N*/20-phenol solution,
50 c.c. *N*/40-sodium thiosulphate.

<i>t.</i>	<i>a-z.</i>	<i>k.</i>	<i>t.</i>	<i>a-z.</i>	<i>k.</i>
109	7.91	0.3120×10^{-5}	253	6.69	0.3083×10^{-5}
258	6.51	0.3390	398	5.79	0.3477
409	6.17	0.2656	609	5.09	0.3604
533	5.53	0.3074	779	4.71	0.3680
644	5.10	0.3384	933	4.40	0.3835
785	4.71	0.3631	1075	4.35	0.2815
929	4.47	0.3658	1349	3.86	0.4049
1060	4.30	0.3640	1414	3.88	0.3631
1163	4.06	0.4032			
Mean.....		0.3398×10^{-5}	Mean.....		0.3519×10^{-5}

<i>t.</i>	<i>a-z.</i>	<i>k.</i>	<i>t.</i>	<i>a-z.</i>	<i>k.</i>
194	7.19	0.2906×10^{-5}	132	7.80	0.2796×10^{-5}
332	6.21	0.3189	268	6.65	0.3184
493	5.68	0.2995	407	5.75	0.3488
614	5.12	0.3501	537	5.30	0.3548
738	5.09	0.2974	674	5.00	0.3461
909	4.48	0.3710	823	4.66	0.3602
1038	4.33	0.3634	982	4.46	0.3485
1227	3.96	0.4103	1108	4.28	0.3536
1359	3.85	0.4053	1252	4.03	0.3800
Mean.....		0.3452×10^{-5}	Mean.....		0.3322×10^{-5}

Mean of four series, 0.3423×10^{-5} .

(iv) *Ferric Alum, Ethyl Acetoacetate, and Sodium Thiosulphate.*

25 C.c. *N*/20-ferric alum, 25 c.c. 4*N*/20-ethyl acetoacetate, and
50 c.c. *N*/40-sodium thiosulphate.

Considerable difficulty was at first experienced in titrating with *N*/80-iodine, probably on account of reaction of the halogen with the acetoacetate. Mr. A. D. Mitchell suggested that considerable dilution and addition of excess of potassium iodide might obviate the difficulty, and, using this suggestion, fair results were obtained

<i>t.</i>	<i>a-z.</i>	<i>k.</i>	<i>t.</i>	<i>a-z.</i>	<i>k.</i>	<i>t.</i>	<i>a-z.</i>	<i>k.</i>
119	8.44	0.1860×10^{-5}	164	7.31	0.3172×10^{-5}	128	7.78	0.2925×10^{-5}
303	6.45	0.3000	449	5.91	0.2886	302	6.40	0.3106
508	5.47	0.3353	593	5.24	0.3340	444	5.91	0.2886
1025	5.02	0.2694	738	4.99	0.2970	599	5.26	0.3279
1215	4.28	0.3226	1079	4.54	0.2990	952	4.75	0.2918
1408	4.08	0.3244	1255	4.01	0.3854	1322	4.09	0.3434
1644	4.01	0.2943	1395	3.79	0.4248	1457	4.02	0.3293
Mean..		0.2903×10^{-5}	Mean...		0.3381×10^{-5}	Mean...		0.3120×10^{-5}

Mean of three series, 0.3135×10^{-5} .

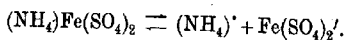
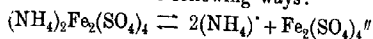
(v) *Other Ferric Compounds.*

Originally it was intended to determine velocity constants for ferric solutions to which other substances than those mentioned above had been added. The homologues of phenol proved to be insufficiently soluble in water and ferric solutions to which four molecular proportions of sodium acetate had been added, whilst reacting slowly, proved quite useless owing to deposition of basic ferric acetate.

The results with acetylacetone were interesting. Solutions containing ferric alum and acetylacetone are very slowly decolorised by sodium thiosulphate; our expectation of measuring the velocity constant with ease was disappointed, for it was found that such solutions were not immediately precipitated by a mixture of sodium thiosulphate and acetate.

Conclusions.

The comparatively slow reduction of ammonia ferric alum as compared with ferric chloride or solutions of ferric thiocyanate containing only a small excess of potassium thiocyanate, point to the iron being present as part of a complex negative ion in such solutions. These ions might arise by dissociation of the ammonium ferrisulphate in one of the two following ways:



Since the reaction is quadrimolecular, two complexes containing iron must react with two thiosulphate ions; hence the second ionisation scheme for the ammonium ferrisulphate appears more probable.

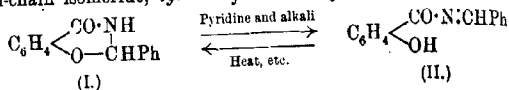
NOTE.—A recent paper by Vorländer (*Ber.*, 1913, **46**, 181) deals with the production of Prussian blue from a ferric salt and ferrocyanide as a time-reaction. The time taken in the production of a precipitate is explained on the ground that ferric salts form incomplete colloidal solutions; whilst this explanation may hold in the case examined by Vorländer, the retardation of many ferric reactions can be explained by the formation of complex negative ions or of very slightly dissociated complexes.

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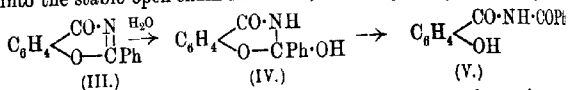
XLI.—Hexahydropyrimidine and its Benzoyl Derivatives.

By ARTHUR WALSH TITHERLEY and GERALD FYRE
KIRKWOOD BRANCH.

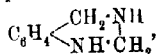
THE object underlying the synthesis of hexahydropyrimidine and its benzoyl derivatives, described in the present paper, was to study the tautomeric relations which it was anticipated would obtain between the cyclic and open-chain forms. It has already been shown by one of the authors (T., 1907, 91, 1423) that reduced oxazine-one derivatives of the type of 2-phenyldihydro-1:3-benzoxazine-4-one (I) may undergo reversible isomeric change to the open-chain isomeride, *syn*-benzylidenesalicylamide (II), thus:



Further (T., 1910, 97, 201), whilst the unsaturated 2-phenyl-1:3-benzoxazine-4-one (III) presents a stable ring *per se* (although easily ruptured by hydrolytic agents), addition of the elements of water gives the unstable saturated ring, 2-hydroxy-2-phenyldihydro-1:3-benzoxazine-4-one (IV), which immediately by rearrangement passes into the stable open-chain isomeride, *N*-benzoylsalicylamide (V):



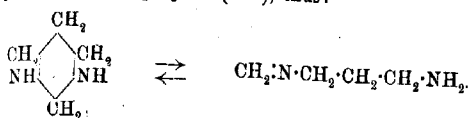
Similar examples of extremely unstable saturated oxazine-one rings which rearrange to the isomeric open-chain forms by wandering of a hydrogen atom have been described among the 2-amino series by Titherley and Hughes (T., 1911, 99, 1493). Similar relations of ring instability might therefore be anticipated among hexahydropyrimidines, in which, as in the reduced oxazines, a similar six-membered ring is present, the oxygen atom having been replaced by the imino-group. Pyrimidines and partly reduced pyrimidines are known to present stable ring systems, and tautomeric or isomeric change involving an open-chain form is generally excluded. With the exception of tetrahydroquinazoline,



described by Busch (*J. pr. Chem.*, 1895, [ii], 51, 129) and Gabriel (*Ber.*, 1903, 36, 811), and allied derivatives, no reduced pyrimidine containing the $\text{NH}\cdot\text{CH}_2\cdot\text{NH}$ -group appear to have been obtained. The compound obtained by Busch and Gabriel, although not strictly

a hexahydropyrimidine derivative, could conceivably rearrange to the open-chain isomeride, $C_6H_4 \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ N:CH_2 \\ | \\ NH_2 \end{smallmatrix}$, and it is possible that this formula appears in the monohydrochloride, $C_6H_{10}N_2 \cdot HCl$ (*loc. cit.*), which it yields. Further work will be carried out to throw light on this point.

With the hitherto unknown simple hexahydropyrimidine (VI) it has been shown by the authors that tautomerism exists, involving make and break of the cyclic form, and producing the open-chain methylene- $\alpha\gamma$ -diaminopropane (VII), thus:

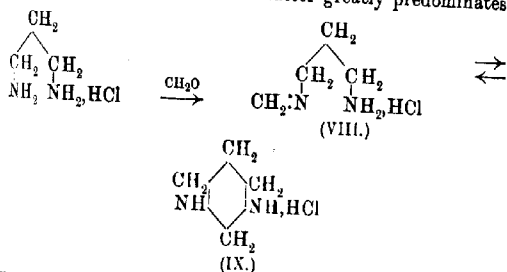


(VI) Hexahydropyrimidine.

(VII.) Methylene- $\alpha\gamma$ -diaminopropane.

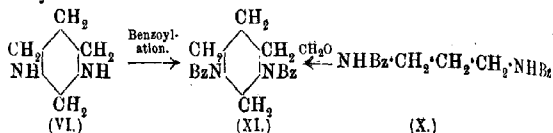
Considerable difficulties were encountered in the synthesis of this tautomeric substance, which was obtained by the condensation of $\alpha\gamma$ -diaminopropane and formaldehyde, partly because of its easy hydrolysis by acids and partly because of the above reversible change. The condensation of $\alpha\gamma$ -diaminopropane and formaldehyde has already been studied by Bischoff and Reinfeld (*Ber.*, 1903, **36**, 35), who obtained ill-defined mixtures containing oxygen and apparently an impure dimethylene derivative, $CH_2 \cdot N[CH_2]_3 \cdot N \cdot CH_2$, owing to the fact that the reaction was not sufficiently controlled, condensation having occurred in several possible ways, as might be expected between such chemically reactive materials.

The authors have found, however, that by the action of aqueous formaldehyde on $\alpha\gamma$ -diaminopropane monoacetate or monohydrochloride simple condensation takes place, yielding an equilibrium mixture of salts (VIII and IX) of hexahydropyrimidine and its open-chain isomeride, in which the latter greatly predominates:



This mixture on benzylation in the presence of alkali functions exclusively as hexahydropyrimidine (VI), and gives an almost

quantitative yield of 1:3-dibenzoylhexahydropyrimidine (XI), which has also been obtained in small yield by the condensation of formaldehyde and dibenzoyl- γ -diaminopropane (X) in the presence of hydrochloric acid:

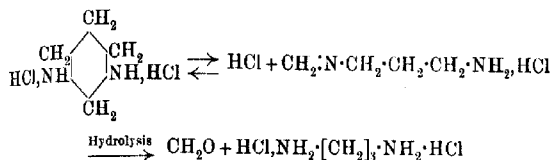


When the above equilibrium mixture of salts is treated with alkali and extracted with ether a mixture of the two bases (VI and VII) is obtained, which on distillation yields a mobile, colourless liquid passing over at about 150°, leaving behind, with rising boiling point, a non-volatile, syrupy residue, which chars if attempts are made to distil it. The volatile fraction, however, rapidly undergoes isomeric change, and if redistilled it leaves behind a considerable fraction of the same syrupy substance, which is evidently methylene- γ -diaminopropane. Moreover, it is slowly but completely changed into the same syrupy substance on keeping in contact with solid potassium hydroxide. It is clear from these facts that the tautomeric relation between the two bases is complicated by polymerisation. It is probable that the distillate boiling at 150° consists essentially of the cyclic base (VI) in equilibrium with small quantities of the open-chain isomeride (VII) and polymeric forms of the latter. On concentration (distillation) progressive polymerisation of the open-chain form takes place, in a similar manner to that of aqueous solutions of formaldehyde. The syrupy mixture of polymerides so obtained is readily soluble in water, with depolymerisation, yielding a strongly alkaline solution, evidently identical with the aqueous solution of the volatile distillate, since both on benzoylation yield the same 1:3-dibenzoylhexahydropyrimidine.

The behaviour of the mixture of bases in aqueous solution with hydrochloric acid is very striking. On titration to the neutral point with methyl-orange a value is obtained corresponding approximately with the monacidic open-chain base, but it is possible by gradual further addition of acid to obtain a value corresponding approximately with the diacidic cyclic base, and it would appear, therefore, that the stable form in the presence of two equivalents of acid is the salt of hexahydropyrimidine, the open-chain salt being present only to a very small extent.* This point, however, is

* These observations recall those of Titherley and Hughes (*loc. cit.*), in which it has been shown that 2-amino-2-phenyldihydrobenzoxazine-4-one derivatives are stable only as salts, and that in the free condition the open-chain isomerides only are stable.

uncertain owing to complication arising through hydrolysis. Although relatively stable in presence of alkali, the base (more probably the open-chain isomeride) is sensitive to hydrogen ions, and on long contact with acid more or less complete hydrolysis, with the formation of α -diaminopropane and formaldehyde, occurs. Unfortunately, no means were found of ascertaining the rate of hydrolysis, and therefore of fixing how far the second neutral point on titration with acid was determined by isomerisation and how far by the production of α -diaminopropane. It was found, however, that the apparent rate of isomerisation is lowered and not raised by excess of acid, and this is possibly due to inhibition of hydrolysis of the ammonium salt of the open-chain form in the partly reversible relation:

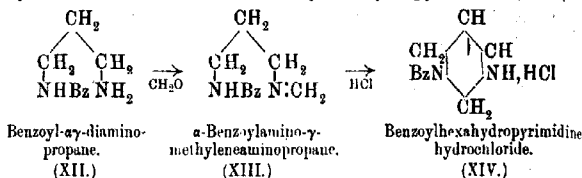


Although this point has not been satisfactorily elucidated, evidence of the formation and existence of the cyclic dihydrochloride in the solution containing two equivalents of hydrochloric acid was obtained in the attempts to isolate the pure salt by evaporation in a vacuum, and by precipitating concentrated aqueous solutions with alcohol. In all cases the solid consisted of a mixture of the dihydrochlorides of hexahydropyrimidine and α -diaminopropane. Owing to partial hydrolysis it was found impossible to prepare any salt of hexahydropyrimidine in a pure condition.

In order to throw further light on hexahydropyrimidine tautomerism, attention was turned to the benzoyl derivatives. The dibenzoyl derivative already mentioned, in which both mobile hydrogen atoms are substituted, is, as would be expected, perfectly stable. Monobenzoylhexahydropyrimidine containing still a mobile hydrogen atom was next synthesised. It could not be obtained by incomplete benzoylation of the mixed bases, but was prepared by the condensation of formaldehyde and benzoyl- α -diaminopropane (XII), the synthesis of which from 2-phenyl-1:4:5:6-tetrahydropyrimidine by the authors has been described in a previous paper (T., 1912, 101, 2348).

The product of the condensation is an amorphous, colourless solid with perfectly neutral properties, but on treatment with acid it rapidly combines with the latter to the extent of one equivalent. There can be no doubt, therefore, that this pseudo-base is α -benzoyl-

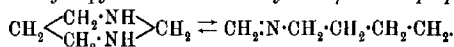
amino- γ -methyleneaminopropane (XIII), and that the salt is the hydrochloride of the isomeric benzoylhexahydropyrimidine (XIV):



The hydrochloride (XIV), unlike the dihydrochloride of hexahydropyrimidine, is quite stable, and rapidly crystallises in a pure form. This stability appears to be due to the fact that the hypothetical cyclic (pseudo) base is a strong one, and that its dissociation constant is much higher than the second dissociation constant of hexahydropyrimidine. With hexahydropyrimidine dihydrochloride some salt-hydrolysis takes place, yielding the monohydrochloride (IX), which at once comes into tautomeric equilibrium with the open-chain hydrochloride (VIII); the latter being sensitive to hydrogen ions, then, suffers hydrolysis, as previously described.

EXPERIMENTAL.

Hexahydropyrimidine and Methylene- α -diaminopropane,



The synthesis of this tautomeric compound was effected by the action of aqueous formaldehyde on α -diaminopropane monohydrochloride. An aqueous solution, of about 25 per cent. concentration, of the diamine, was divided in equal portions; one was neutralised exactly (using methyl-orange as indicator) with dilute (*N*/10) hydrochloric acid, and the other was then added. To the resulting aqueous solution of the monohydrochloride a solution of formaldehyde (1 mol.) of previously ascertained concentration was added very slowly drop by drop with continual agitation. Rapid action and disappearance of free formaldehyde took place at first, but as the rate of action fell off, care was taken to add the formaldehyde solution more slowly so as to avoid excess. The total time occupied in the addition was about an hour for 2.4 grams of α -diaminopropane hydrochloride. A clear, odourless solution resulted, which was neutral towards phenolphthalein, but alkaline towards litmus and methyl-orange. This solution consists essentially of the hydrochloride of methylene- α -diaminopropane. In the same way the acetate and oxalate were obtained from the corresponding mono-salts of α -diaminopropane.

Isolation of the Free Base.—The aqueous solution containing the hydrochloride was treated in the cold with solid potassium hydroxide in excess, when a colourless oil was precipitated, which was extracted with ether. The ethereal solution, after keeping for three hours over solid potassium hydroxide, on distilling, to remove the ether, left a light oil, but some of the base passed over with the ether. The light oil on fractionation gave a mobile, colourless distillate (about two-thirds of the total), boiling between 140° and 160° , and left a slightly discoloured syrup which began to darken above 220° without distilling. The volatile fraction was then immediately redistilled, and behaved in the same way as the original liquid, yielding a mobile liquid boiling between 140° and 160° , and leaving about the same proportion of non-volatile syrup. This syrup, evidently the polymerised form of methylene- α -diaminopropane, fumed slightly in the air, and dissolved at once in water, yielding a strongly alkaline solution, which on benzylation gave 1:3-dibenzoylhexahydropyrimidine, as an oil which solidified on keeping, and melting, after recrystallisation from aqueous alcohol, at 93° . A mixture with a specimen (1) obtained by benzylation of the volatile fraction (see below), and (2) by benzylation of methylene- α -diaminopropane acetate (p. 334), melted at 93 – 94° in each case. In all other respects the aqueous solution of the syrup appeared to be identical with that of the volatile fraction; it yielded the same picrate mixture (p. 337), and showed the same behaviour on treatment with acid, as described below. The volatile fraction fumed strongly in the air, and possessed a peculiar basic odour and powerful basic properties. It was extremely hygroscopic, and on this account it was impossible to obtain an accurate analysis. After remaining for a short time over solid potassium it contained $N=29.86$. On prolonged keeping over solid potassium hydroxide the mobile liquid gradually changes to a colourless, viscid syrup similar to that obtained by distillation. On passing air free from carbon dioxide, but containing minute traces of moisture, over the mobile liquid, water was taken up to the extent of about 1 molecular proportion, yielding apparently an ammonium hydroxide as a slightly syrupy liquid:

0.0756 , by Kjeldahl's method, required 14.45 c.c. $N/10\text{-HCl}$.

$N=26.76$.

$C_4H_{10}N_2 \cdot H_2O$ requires $N=26.90$ per cent.

$C_4H_{10}N_2$ requires $N=32.56$ per cent.

An aqueous solution of the base on benzylation by benzoyl chloride and alkali gave 1:3-dibenzoylhexahydropyrimidine, in needles melting, after recrystallisation from aqueous alcohol, at 94° , identical with the compound described above and on p. 339.

The behaviour of the base with dilute hydrochloric acid was investigated with the object of studying its tautomeric relations and hydrolysis; and attempts were also made to prepare a solid hydrochloride. An aqueous solution of the undistilled base was prepared by shaking the ethereal solution obtained as described on p. 335 with water, which very readily dissolves it. The concentration of this aqueous solution was ascertained by boiling with an excess of *N*/10-hydrochloric acid for thirty minutes, to hydrolyse it completely to trimethylenediamine, and titrating back the excess of acid. As 1 c.c. of this solution after hydrolysis required 4.5 c.c. of *N*/10-hydrochloric acid, corresponding with two basic nitrogen atoms, it follows that 1 c.c. of this solution should require 4.5 c.c. of *N*/10-hydrochloric acid if on neutralisation it gave hexahydropyrimidine dihydrochloride entirely, and 2.25 c.c. of *N*/10-hydrochloric acid if it gave the hydrochloride of methylene- α -diaminopropane entirely. Since 1 c.c. of this solution (0.225 molar concentration) at 21° required 2.5 c.c. of *N*/10-hydrochloric acid, using methyl-orange, to reach the first neutral point, it follows that the latter corresponds with a proportion of about 89 per cent. of the open-chain hydrochloride and 11 per cent. of the cyclic monohydrochloride in the equilibrium mixture. The effect of further gradual addition of hydrochloric acid to this neutral solution is to give an acid solution, which becomes neutral, rapidly at first, but more slowly as the second neutral point, which corresponds with the addition of about 2 c.c. of *N*/10-hydrochloric acid, is neared. The second neutral point thus corresponds with two equivalents of hydrochloric acid, combined partly with hexahydropyrimidine and partly with α -diaminopropane hydrolytically formed.

The effect on the second neutral point of excess (more than one equivalent) of acid on keeping was examined at 21° by adding 1 c.c. of the above aqueous solution of the base to varying amounts of *N*/10-hydrochloric acid, and titrating back after known intervals of time with *N*/10-sodium hydroxide. Similar experiments were made with *N*/10-sulphuric acid.

It was found that excess of acid, instead of accelerating the rate at which the second neutral point approaches that corresponding with the neutralisation of two equivalents, retards it. This point is, in fact, most rapidly attained when the base is gradually treated with acid so as to avoid appreciable excess of the latter. Attempts were made to ascertain the extent of hydrolysis by benzylation, after keeping with acid for varying lengths of time. In no case, however, could any dibenzoyl- α -diaminopropane be obtained, and always 1:3-dibenzoylhexahydropyrimidine resulted, but this fact, which at first suggested that no hydrolysis had occurred, might be

due to the recombination of α -diaminopropane and formaldehyde occurring during the Schotten-Baumann process. Moreover, free formaldehyde was shown by the well known colour tests, but it was not found possible to utilise these tests quantitatively. An attempt roughly to gauge the extent of hydrolysis was next made by evaporating solutions, obtained from the base by addition of hydrochloric acid, at laboratory temperatures, in a vacuum over potassium hydroxide and sulphuric acid, and fixing the composition of the resulting solid by analysis. In all cases the solid proved to be a mixture containing α -diaminopropane dihydrochloride. An odour of formaldehyde was also detected, showing that hydrolysis had occurred.

The following values showing the percentage of chlorine in the solid were obtained:

(1)	After evaporation with one equivalent of HCl.....	Cl = 33.39
(2)	" " " " " " HCl.....	Cl = 32.96
(3)	" " " " " " with two equivalents of HCl.....	Cl = 45.56
(4)	" " " " " " " " HCl.....	Cl = 46.41

(1) and (2) Methylene- α -diaminopropane hydrochloride requires
Cl = 28.98 per cent.

α -Diaminopropane monohydrochloride requires Cl = 32.13 per cent.

(3) and (4) Hexahydropyrimidine dihydrochloride requires
Cl = 44.67 per cent.

α -Diaminopropane dihydrochloride requires Cl = 48.29 per cent.

Solids 1 and 2 on extracting with alcohol, in which methylene- α -diaminopropane hydrochloride and α -diaminopropane monohydrochloride are soluble, left a considerable residue (48 per cent.) of insoluble α -diaminopropane dihydrochloride. (Found: (1) Cl = 47.79; (2) Cl = 47.33. Calc., Cl = 48.29 per cent.)

It follows from these analytical data that considerable hydrolysis had taken place (to the extent of 30 per cent. in 3 and to a further extent in the others), but forty-eight hours had elapsed during the evaporation. An attempt was next made to precipitate the dihydrochloride of hexahydropyrimidine by adding excess of alcoholic hydrogen chloride to a concentrated solution of the monoacetate of the base obtained as described on p. 334. A white, crystalline solid separated, which contained Cl = 47.17 per cent. This corresponds with a mixture of 30 per cent. of hexahydropyrimidine dihydrochloride and 70 per cent. of α -diaminopropane dihydrochloride, and on benzylation it yielded a considerable quantity of dibenzoyl- α -diaminopropane (m. p. 146°). All attempts to prepare any pure salt of hexahydropyrimidine have so far failed. The *picrate* was obtained on adding aqueous picric acid to a solution of the base as a yellow, microcrystalline precipitate, melting at

186° to a turbid liquid. It was insoluble in water or alcohol, and was evidently a mixture of the mono- and di-picrates;

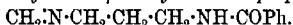
0.0756 gave 14.10 c.c. N_2 (moist) at 21° and 764 mm. $N = 21.38$.

Methylene- α -diaminopropane picrate requires $N = 22.22$ per cent.

Hexahydropyrimidine dipicrate requires $N = 20.59$ per cent.

An equimolecular mixture requires $N = 21.19$ per cent.

α -Benzoylamino- γ -methyleaminopropane,

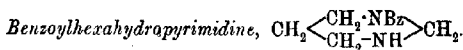


This compound in a polymerised form was obtained from monobenzoyl- α -diaminopropane (T., 1912, 101, 2350) by condensation with formaldehyde. One gram of the normal oxalate of this base, dissolved in the minimum quantity of water, was treated with one equivalent of $N/10$ -sodium hydroxide, and the calculated quantity of formaldehyde was gradually added to the clear aqueous solution. A colourless oil was immediately precipitated, which was extracted with pure ethyl acetate. The solution, after remaining a short time over solid potassium hydroxide, was then evaporated and kept in a vacuum for several days. A clear oil remained, which gradually changed to a practically solid, transparent, glassy, amorphous, and brittle mass, weighing 0.72 gram (theory requires 0.85 gram), which showed no tendency to crystallise:

0.1130, by Kjeldahl's method, required 11.7 c.c. $N/10$ -HCl.
 $N = 14.58$.

$C_{11}H_{14}ON_2$ requires $N = 14.74$ per cent.

The amorphous solid is insoluble in water, very soluble in alcohol, moderately so in benzene, sparingly so in ether, and insoluble in light petroleum. On heating with excess of water for several hours it slowly passes into solution, with hydrolysis, forming a clear, alkaline solution containing monobenzoyl- α -diaminopropane and formaldehyde, which can be detected by its odour. On cooling, recombination takes place, α -benzoylamino- γ -methyleaminopropane being precipitated as an emulsion. On treatment with cold water and phenolphthalein, it shows a perfectly neutral reaction, but it immediately dissolves in acids, with rearrangement, forming salts of benzoylhexahydropyrimidine.



The free base is unknown, and on liberation from its salts by alkali, undergoes immediate reverse rearrangement to the above open-chain isomeride, which is obtained as an insoluble oil. The *hydrochloride*, obtained by exact neutralisation by aqueous hydro-

chloric acid of α -benzoylamino- γ -methyleneaminopropane in aqueous alcoholic solution, on evaporation in a vacuum, crystallises in colourless needles, sparingly soluble in alcohol:

0.0843 gave 0.0534 AgCl. Cl=15.68.

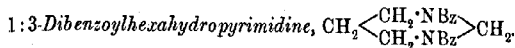
$C_{11}H_{14}ON_2 \cdot HCl$ requires Cl=15.67 per cent.

The *platinichloride* is precipitated slowly from dilute aqueous solution in clusters of orange needles, melting and decomposing at 202–203°:

0.1634 gave 0.0410 Pt. Pt=25.09.

$(C_{11}H_{14}ON_2 \cdot HCl)_2PtCl_4$ requires Pt=25.06 per cent.

The *picrate* and *oxalate* could not be obtained crystalline. The *acetate* slowly crystallises on evaporation in air.



Attempts to obtain this compound, by the Schotten-Baumann benzoylation of α -benzoylamino- γ -methyleneaminopropane, failed apparently because of the highly insoluble polymerised nature of the latter, and only benzoic anhydride resulted.

The compound, however, was easily obtained in the wet benzoylation of the mixed bases (methylene- $\alpha\gamma$ -diaminopropane and hexahydropyrimidine) as already described (p. 335). It was most conveniently prepared direct from either the hydrochloride or acetate of the open-chain base obtained (p. 334) by the action of formaldehyde on the mono-salt of $\alpha\gamma$ -diaminopropane. On merely shaking with benzoyl chloride and alkali a 97 per cent. yield of the dibenzoyl derivative was obtained as an oil, which set to a crystalline solid on keeping. On recrystallisation from aqueous alcohol it formed coarse, transparent, colourless needles, melting at 95°:

0.1582 gave 12.9 c.c. N_2 (moist) at 16° and 756 mm. N=9.46.

0.3331, by Kjeldahl's method, required 22.48 c.c. $N/10\text{-HCl}$. N=9.45.

0.3025, by Kjeldahl's method, required 20.38 c.c. $N/10\text{-HCl}$. N=9.43.

$C_{18}H_{18}O_2N_2$ requires N=9.52 per cent.

The same compound was prepared by the condensation of formaldehyde and dibenzoyl- $\alpha\gamma$ -diaminopropane, the latter being dissolved in sufficient concentrated hydrochloric acid and treated with an excess of 40 per cent. formaldehyde. After six days the solution was diluted and left, when the compound slowly crystallised in needles (m. p. 94°), and a further crop (m. p. 93°) was obtained by

neutralising the acid mother liquor with alkali; the total yield was 75 per cent. of the theoretical.

1:3-Dibenzoylhexahydropyrimidine is insoluble in water or light petroleum, very soluble in alcohol, acetone, acetic acid, or chloroform; sparingly so in cold benzene, ether, or carbon tetrachloride, and moderately so in hot benzene. It is moderately soluble in cold concentrated hydrochloric acid or 98 per cent. sulphuric acid, without decomposition. It is slowly hydrolysed by heating with aqueous mineral acids, yielding benzoic acid, formaldehyde, and α -diaminopropane, which was identified as its dibenzoyl derivative. The hydrolysis is incomplete with concentrated hydrochloric acid at 80° in seven and a-half hours, but complete after heating a further two hours at 100°. On boiling with 10 per cent. sodium hydroxide, two molecules of benzoic acid are eliminated, and methylene- α -diaminopropane, largely undecomposed, is produced; on benzoylating the product after complete hydrolysis a good yield of the original compound is obtained.

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XLII.—*The Interaction of Bromine and the Sulphides of β -Naphthol. Part II.*

By THOMAS JOSEPH NOLAN and SAMUEL SMILES.

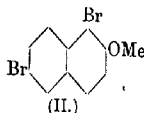
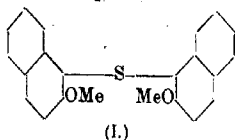
IN the first part of this investigation (T., 1912, 101, 1420) it was shown that with bromine the stable sulphide of β -naphthol yields 1:6-dibromo- β -naphthol, sulphur being displaced by the halogen, whilst the unstable sulphide yields a derivative of dibromonaphthasulphonium-quinone. Thence the inference was made that the hydroxy- and thio-groups of the unstable sulphide respectively occupy positions 2 and 1 in the naphthalene nucleus which are the same as those occupied in the stable sulphide. Moreover, since the halogen in the bromonaphthasulphonium-quinone is situated in the quinonoid portion of the naphthalene nucleus, it is of some importance to determine whether this substitution by halogen takes place before or after conversion to the quinonoid structure, for in the former circumstance valuable information with regard to the structure of the unstable sulphide would be at hand.

The experiments described in the following pages were originally undertaken with this end in view, and accordingly the interaction of bromine and the acyl and alkyl derivatives of the two sulphides

has been examined with the hope that with these derivatives of the unstable sulphide substitution would take place without other disturbance.

Derivatives of the Stable Sulphide.

The methyl ether of β -naphthol sulphide (I) was obtained by the interaction of sulphur chloride and the methyl ether of β -naphthol :



Other means of obtaining this substance were employed with unsatisfactory results, and the experience met with serves as further illustration (*loc. cit.*) of the ease with which the stable sulphide of β -naphthol loses sulphur from the α -position; thus methylation with methyl sulphate in alkaline solution proceeds very sluggishly, and if the conditions are intensified sulphur is partly eliminated in the form of methyl sulphide and other products. Also, when the silver salt of β -naphthol sulphide is treated with methyl iodide, the interaction is complex; partial oxidation to the sulphonium-quinone takes place whilst methyl sulphide is abundantly formed. However, the method first described furnishes excellent yields of the required substance.

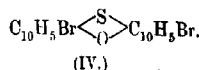
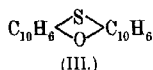
When this methyl ether is suspended in cold glacial acetic acid and treated with eight atomic proportions of bromine, a rapid interaction takes place, and the methyl ether of 1:6-dibromo- β -naphthol (II) is formed in almost quantitative yield whilst sulphur is eliminated. The acetyl derivative of β -naphthol sulphide exhibits considerably greater stability towards this reagent than the methyl ether, for when it is suspended in a cold solution of bromine in acetic acid scarcely any interaction takes place even during the lapse of six or seven hours. Also, when a cold solution of this acetyl derivative in acetic anhydride is treated with bromine, the greater portion of the compound ultimately separates unchanged from the medium. Comparison of this behaviour of the acetyl derivative of the stable sulphide with that of the acetylated unstable sulphide shows an emphatic contrast.

Derivatives of the Unstable Sulphide.

Henriques (*Ber.*, 1894, 27, 2999) has stated that the acetyl derivative of the unstable sulphide may be obtained as a yellow, crystalline material, which melts at 148° . Presumably the method which

yielded this substance was the same as that employed in preparing the acetyl derivative of the stable sulphide, namely, prolonged treatment with acetic anhydride and sodium acetate. On repeating this experiment we have found that a substance of this appearance and approximate melting point is formed, but on further examination this has proved to be the anhydride of the unstable sulphide. The substance is dealt with in a subsequent paragraph, and it is sufficient for the present to mention that the required acetyl derivative is a colourless, amorphous substance which is readily obtained from the interaction of the unstable sulphide and cold acetic anhydride in the presence of camphorsulphonic acid.

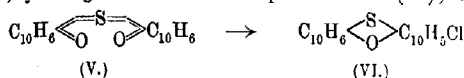
The chief characteristic of this acetyl derivative is the instability of the acyl groups, which are very easily eliminated; thus, for example, treatment with boiling acetic anhydride and sodium acetate under suitable conditions converts the acetyl derivative into the anhydride (III) of the unstable sulphide (P., 1912, **28**, 275):



This substance (III) may also be obtained by the action of other dehydrating agents on the unstable sulphide, and since the latter contains the thio-arrangement and two hydroxyl groups (see p. 346 and T., 1912, **101**, 1420) the formula shown above is assigned to the anhydride, which is provisionally termed *isonaphthathioxin*. Moreover, it may be noticed that although the substance differs in physical character from the naphthathioxin (m. p. 166°) obtained from the stable sulphide (Mauthner, *Ber.*, 1906, **39**, 1340), the chemical characteristics of the two anhydrides are closely similar; thus both yield sulfoxides when treated with nitric acid or thioxonium salts by addition of bromine; the former give chloro-derivatives by reaction with hydrogen chloride, and the latter are converted into bromo-derivatives by heating with certain solvents. A more detailed account and comparison of the two anhydrides and their derivatives will be given in a subsequent paper.

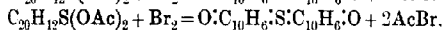
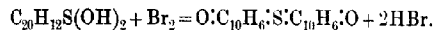
When the anhydride of the unstable sulphide is treated with excess of bromine (at least four atomic proportions) an insoluble, green thioxonium bromide is formed, which on being heated in certain solvents yields the dibromo-derivative (IV) of the *isonaphthathioxin*. In the formula by which this substance is represented, a bromine atom is assigned to each naphthalene nucleus; it seems highly probable that this arrangement is correct, but no direct proof of it can at present be brought forward. The acetyl derivative of the unstable sulphide by treatment with excess

of bromine (eight atomic proportions) in cold acetic acid also is converted into a green thioxonium bromide, which easily yields a dibromonaphthathioxin identical with that obtained by direct bromination of isonaphthathioxin. It is therefore clear that with this reagent the acetyl groups are very easily removed from diacetylnaphthol isosulphide, and the contrast with the behaviour of diacetylnaphthol sulphide clearly shows a profound difference in the structure of these two substances. The result obtained with the acetyl derivative of the unstable sulphide is sufficiently striking to warrant a brief discussion of the probable mechanism of the process. Previous experiments (T., 1912, 101, 715) have shown that β -naphthasulphonium-quinone (V) is easily attacked by acetyl chloride, yielding the monochloronaphthathioxin (VI); and on



substituting acetyl bromide for the chloride we find that a similar product is obtained. The interaction is not so rapid as with the chloride, and the product is a mixture of the mono- and dibromonaphthathioxins which is difficult completely to resolve; but after further bromination the pure dibromonaphthathioxin (IV) was isolated. Moreover, the same substance (IV) is obtained by interaction of excess of bromine and the naphthasulphonium-quinone (V) in cold acetyl bromide or acetic anhydride.

On comparing the behaviour of the unstable sulphide with that of its diacetyl derivative, it is seen that with excess of bromine in cold acetic acid the former gives the dibromonaphthasulphonium-quinone (T., 1912, 101, 1420; also experimental part of this paper), whilst the latter yields the dibromonaphthathioxin. This apparent anomaly can only be explained by the production of naphthasulphonium-quinone in both cases at a preliminary stage of the interaction:



It is then evident that in the former case merely further bromination will take place; but in the latter acetyl bromide is formed simultaneously with the quinone, and, as already mentioned, it may be shown by independent experiment that under these conditions with excess of bromine the quinone yields the dibromonaphthathioxin (IV). Further confirmation of this conclusion is afforded by the fact that the unstable sulphide when treated with this halogen in acetic anhydride yields the same naphthathioxin derivative.

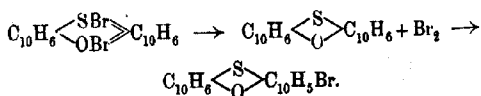
Thus it may be inferred that in these interactions the quinone

is formed before bromination takes place. Moreover, it is necessary to mention that if the reverse were correct the dibromosulphonium-quinone should result, for experiment shows that under the conditions adopted this substance is not converted by bromine and acetic anhydride into the dibromonaphthathioxin. For these reasons it must be admitted that the position taken up by the halogen in the dibromosulphonium-quinone or the dibromonaphthathioxin cannot be legitimately employed as evidence in a discussion of the nature of the unstable sulphide, for it seems, as already pointed out, that these are formed by bromination of the quinone under different conditions. It is, on the other hand, very clear from these experiments that the two sulphides remarkably differ from one another in the character of the hydroxyl groups which they contain.

In summarising the results of these experiments which have dealt with the interaction of bromine and the isomeric sulphides of β -naphthol or their acetyl derivatives, it may be stated that the stable sulphide, the methyl ether, and the acetyl derivative are evidently true derivatives of β -naphthol. On the other hand, it is clear that the unstable sulphide cannot be so regarded; indeed, the hydroxyl groups exhibit the peculiar character of certain unsaturated tertiary alcohols. This question will be more fully discussed when more complete evidence of the character of the substance has been obtained from a study of the *isonaphthathioxin* mentioned in the foregoing pages.

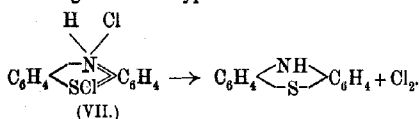
It remains finally to remark that in all these cases where bromination of the naphthathioxin takes place in presence of an excess of the halogen an insoluble thioxonium bromide is formed at the penultimate stage, but the substance may be converted by heat, either in the reacting mixture or separately, into the dibromonaphthathioxin. Unfortunately, this bromide is sufficiently unstable to defy attempts to obtain it in a condition fit for analysis, for, after being freed from excess of bromine and during desiccation, it partly loses bromine and partly undergoes further bromination in the nuclei. A mixture of mono- and di-bromonaphthathioxins is then obtained, in which the former greatly predominates. When heated with some inactive medium the latter change supervenes, and the chief product is the dibromo-derivative.

It seems, therefore, that in the conversion of the thioxonium salt into the bromonaphthathioxins separation of the halogen takes place before bromination of the nucleus, for example:



Regarded independently, this conclusion is of little importance, but it throws some light on the analogous case of the interaction of phenazothionium chloride and hot hydrogen chloride.

The products here obtained (Page and Smiles, T., 1910, 97, 1112) are mono- and di-chlorothiodiphenylamine, and the fact that the mixture is produced is sufficient to indicate that the process is not a simple intramolecular change. It has been observed (*loc. cit.*) that the presence of hydrogen chloride is indispensable to the reaction, and the behaviour of the thioxonium salts now recorded lends further weight to the hypothesis that the final chlorination



due to the separation of halogen from the dichloride (VII) of the phenazothionium base.

EXPERIMENTAL.

Derivatives of the Stable Sulphide.

The Dimethyl Ether, $\text{MeO} \cdot \text{C}_{10}\text{H}_6 \cdot \text{S} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OMe}$.—A solution of sulphur dichloride in dry chloroform was gradually added to a cold concentrated solution of two molecular proportions of β -naphthol methyl ether in the same solvent. Interaction took place at once, hydrogen chloride being rapidly evolved, and after the mixture had been kept at the atmospheric temperature for three hours the required substance had almost completely separated in the crystalline state. The yield of the crude product obtained in this manner was almost quantitative. It was recrystallised from a large volume of boiling acetone, and after being dried was analysed:

0.1019 gave 0.2841 CO_2 and 0.0492 H_2O . $\text{C} = 76.0$; $\text{H} = 5.3$.

$\text{C}_{22}\text{H}_{18}\text{O}_2\text{S}$ requires $\text{C} = 73.3$; $\text{H} = 5.2$ per cent.

The dimethyl ether of β -naphthol sulphide forms pale yellow needles, which melt at 184° , and are sparingly soluble in most cold organic media. Like the hydroxy-derivative, it readily dissolves in concentrated sulphuric acid, giving an intensely blue solution.

Reaction with Bromine.—The finely powdered substance was added to a cold solution of eight atomic proportions of bromine in cold glacial acetic acid. The mixture was kept at the atmospheric temperature, and shaken at frequent intervals. The sulphide gradually dissolved, and after the lapse of about three hours, when solution was complete, the reacting liquid was poured into a large bulk of water, the solid precipitate being subsequently collected.

The product was recrystallised from alcohol, and, by a close comparison with the product of methylation of 1:6-dibromo- β -naphthol (Davis, T., 1900, 77, 37) or of bromination of β -naphthyl methyl ether, was identified as the methyl ether of 1:6-dibromo- β -naphthol. It melted at 100°, whether heated alone or mixed with the substance obtained from these sources.

Diacetyl Derivative, $\text{AcO} \cdot \text{C}_{10}\text{H}_6 \cdot \text{S} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OAc}$.

This substance has been described by Henriques (*Ber.*, 1894, 27, 2990), who obtained it by acetylating the dihydroxy-compound with acetic anhydride in presence of sodium acetate. The preparation may be more efficiently carried out by heating to 80° the hydroxy-sulphide with acetic anhydride and a small quantity of camphor-sulphonic acid. Experiments were made on the behaviour of this substance with bromine under the same conditions as adopted in the treatment of the acetyl derivative of the unstable sulphide. The finely powdered substance was suspended in cold glacial acetic acid, and treated with eight atomic proportions of bromine. No definite interaction could be detected, for, after the reacting mixture had been kept for one hour at the atmospheric temperature with frequent agitation, almost the whole of the original acetyl derivative was recovered unchanged. Further, a warm solution of this acetyl derivative in acetic anhydride was mixed with eight atomic proportions of bromine, and when this was set aside the greater portion of the original material separated unchanged. It will be seen from experiments described in subsequent paragraphs that the behaviour of the acetyl derivative of the unstable sulphide is profoundly different; this substance is immediately attacked by the reagent under the same conditions.

Derivatives of the Unstable Sulphide.

Evidence showing the presence of two hydroxyl groups in the unstable sulphide has already been adduced by Henriques (*loc. cit.*), who prepared and analysed the lead salt of this substance. Further data supporting this conclusion have now been obtained by estimating the active hydrogen available for reaction with magnesium methyl iodide (Hibbert and Sudborough, P., 1904, 19, 285; Zerewetinoff, *Ber.*, 1907, 40, 2023; 1908, 41, 2233):

0.0730 gave 10.03 c.c. CH_4 at 0° and 760 mm. $\text{OH} = 10.76$.

$\text{C}_{20}\text{H}_{12}\text{S}(\text{OH})_2$ requires $\text{OH} = 10.69$ per cent.

The same conclusion is furnished by the existence of a diacetyl derivative.

Diacetyl Derivative of the Unstable Sulphide.—The acetyl deriv

ative of this sulphide has been described by Henriques (*loc. cit.*, p. 3002) as occurring in yellow needles which melt at 148° . The method of preparing this substance was not described, but it seems probable that the process employed was that of prolonged heating with acetic anhydride and sodium acetate which was used in obtaining the acetyl derivative of the stable sulphide. Applying this method we have obtained a substance approximately agreeing with that mentioned by Henriques, but it is the anhydride of the hydroxy-derivative, and is apparently formed by secondary decomposition of the required acetyl compound.

The latter substance is not easily obtained in the pure condition, but after many trials we find that the best method is as follows:

Five grams of the sulphide were suspended in 70 c.c. of cold acetic anhydride, and 1 gram of camphorsulphonic acid was added to the mixture. The sulphide gradually dissolved, and after the mixture had been kept at the atmospheric temperature for four hours acetylation was complete. The reacting liquid was decomposed with ice-cold water; then the insoluble acetyl derivative was collected and purified by precipitating with water from the cold alcoholic solution. The latter operation must be cautiously effected, otherwise the substance may separate in an oily mass; also it may be observed that the success of the preparation largely depends on the purity of the sulphide employed. The product thus obtained is a colourless, amorphous solid, which liquefies at about 75° ; on cooling it re-solidifies to a colourless, glass-like material. For analysis it was dried at 100° :

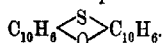
0.1188 gave 0.3100 CO_2 and 0.0478 H_2O . $\text{C}=71.2$; $\text{H}=4.4$.

$\text{C}_{24}\text{H}_{18}\text{O}_4\text{S}$ requires $\text{C}=71.6$; $\text{H}=4.4$ per cent.

On hydrolysis with acids and subsequent distillation of the mixture, the substance yielded acetic acid. It is immediately attacked by cold alcoholic ammonia, and from the alkaline liquid the stable sulphide of β -naphthol was obtained. The formation of the latter compound is to be expected, for the unstable sulphide is converted into the stable by alkaline reagents. Another substance insoluble in aqueous alkaline media was isolated from this interaction, but it has not yet been further examined.

The diacetyl derivative is readily soluble in most organic media and insoluble in water.

Anhydride of the Unstable Sulphide or isoNaphthathioxin,



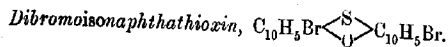
A solution of 5 grams of the acetate of the unstable sulphide and 5 grams of freshly fused sodium acetate in about 75 c.c. of acetic

anhydride was boiled under reflux. The solution gradually assumed a yellow colour, and heating was continued until a sample yielded a semi-crystalline mass on treatment with water. The maximum yield is usually attained after about seventeen hours; more prolonged heating is not advisable, since further decomposition then occurs, and the product is more difficult to isolate. After a suitable period the reacting liquid was allowed to cool, when a mixture of the required substance with sodium acetate separated in the crystalline state. This was collected, and the sodium acetate removed by washing with water. The yield of the crude product thus obtained varied from about 80 per cent. in one experiment to about 10 per cent.; that usually obtained was about 40 per cent., but the most favourable conditions have not yet been definitely ascertained. The substance was purified by crystallisation from glacial acetic acid, with the addition of animal charcoal if necessary; it was then obtained in lemon-yellow needles, which melted at 152° :

0.1086 gave 0.3172 CO_2 and 0.0394 H_2O . $\text{C}=79.66$; $\text{H}=4.0$.
 $\text{C}_{20}\text{H}_{12}\text{OS}$ requires $\text{C}=80.00$; $\text{H}=4.0$ per cent.

It may be recalled that dehydration of the stable sulphide of β -naphthol yields naphthathioxin (Mauthner, *Ber.*, 1906, **39**, 1340; Christopher and Smiles, *T.*, 1912, **101**, 713), which melts at 166° . This is not the same as the substance now described; in fact, a mixture of the two in approximately equal quantities melts indefinitely at about 120° ; moreover, each substance furnishes a distinct series of derivatives (P., 1912, **28**, 275). However, in their chemical nature the two anhydrides resemble one another very closely; indeed, so far as experiment has yet been carried, no clear distinction of this kind has been observed. The substance now described has therefore been termed *isonaphthathioxin*; a fuller investigation of the two series will be soon completed.

The mother liquors from this preparation were examined, and found to contain a further small quantity of the anhydride, the bulk of the dissolved material being the unchanged acetyl derivative. In some experiments a very small quantity of the acetyl derivative of the stable sulphide was isolated and identified in the usual manner. The occurrence of this substance is of some interest, for it seems to show that the unstable acetylated sulphide may be partly transformed into the stable one by the action of heat; whilst the only other means of passing from the unstable to the stable sulphide hitherto recorded is by the influence of alkali hydroxide.



(a) *From isoNaphthathioxin.*—A solution of the anhydride of the unstable sulphide in warm glacial acetic acid was mixed with rather more than four atomic proportions of bromine. The sparingly soluble thioxonium salt was at once precipitated, but on boiling the liquid it was rapidly converted into a mass of yellow needles. These were collected and purified by crystallisation from hot carbon tetrachloride, when *dibromoisonaphthathioxin* was obtained in a mass of yellow, thread-like crystals, which melted at 245° :

0.1015 gave 0.1943 CO_2 and 0.0214 H_2O . $\text{C}=52.2$; $\text{H}=2.3$.

0.1325 „ 0.1088 AgBr . $\text{Br}=34.9$.

$\text{C}_{20}\text{H}_{10}\text{OBr}_2\text{S}$ requires $\text{C}=52.4$; $\text{H}=2.18$; $\text{Br}=34.9$ per cent.

The substance is very sparingly soluble in most cold organic media, and moderately so in hot tetrachloroethane or acetic anhydride. When warmed with concentrated sulphuric acid, it gives a green solution—a colour reaction which is characteristic of this series. The same substance may be readily obtained by several other methods, of which the following are brief descriptions:

(b) *By Interaction of Bromine and the Acetyl Derivative of the Unstable Sulphide.*—A solution of 5 grams of the acetyl derivative in cold glacial acetic acid was gradually mixed with eight atomic proportions of bromine. The precipitated thioxonium salt was collected, and after being freed from excess of bromine by washing with cold acetic acid, it was treated with the boiling medium. When conversion into the yellow bromo-derivatives was complete, the liquid was cooled and the insoluble, crystalline material was collected. By fractional crystallisation from boiling acetic acid a less soluble portion was obtained, and this was found to be dibromoisonaphthathioxin (m. p. 245°); it was identical with the substance formed by bromination of *isonaphthathioxin*. The more soluble part of the product melted at about 176° ; analysis showed that this substance consisted chiefly of the monobromonaphthathioxin, but this was contaminated with the dibromo-derivative, which could not be completely removed from the small quantity of material available. Further bromination (see later paragraph) of this substance yielded the pure dibromo-derivative. When the thioxonium bromide obtained in this interaction is treated with boiling acetic acid bromine is liberated, and it seems probable that loss of halogen in this manner may lead to the formation of a small quantity of the monobromo-derivative. If the salt is kept in a vacuum desiccator for twenty-four hours, conversion into the bromo-

naphthathioxins takes place, whilst bromine is liberated. Under these conditions the amount of the dibromo-derivative formed is relatively smaller, and that of the monobromo-compound is relatively larger, but also in this case complete purification of the latter substance was not attained.

It may be mentioned that this difficulty experienced in obtaining the more soluble halogen derivative in a pure condition from a mixture of two has been previously met with in the mono- and di-chloro-derivatives of thiodiphenylamine (Unger and Hofmann, *Ber.*, 1896, **29**, 1362; Page and Smiles, *T.*, 1910, **97**, 1116).

The yield of the bromonaphthathioxins from 5 grams of the acetyl derivative was about 2 grams, but this may be greatly improved by substituting acetic anhydride for acetic acid as the medium for bromination.

(c) *By Interaction of Bromine and the Unstable Sulphide.*—Previous experiments have shown that the unstable sulphide reacts with bromine in acetic acid, yielding the dibromosulphonium-quinone (*T.*, 1912, **101**, 1420); but if acetic anhydride is employed as the solvent the bromonaphthathioxins are exclusively formed. The conditions adopted and the results obtained were precisely similar to those described in the foregoing paragraphs.

(d) *By Interaction of Bromine and Naphthasulphonium-quinone.* Five grams of the quinone were suspended in 50 c.c. of cold acetic anhydride, and eight atomic proportions of bromine were slowly added to the mixture. On the first addition of bromine the quinone rapidly dissolved, and subsequently the contents of the flask solidified to a mass of the green thioxonium bromide. A dibromonaphthathioxin, identical with that previously described, was isolated from this salt by the process already mentioned. The yield of the crude bromo-derivative was approximately equal in weight to the quinone taken. The interaction of β -naphthasulphonium-quinone and four atomic proportions of bromine in glacial acetic acid has been previously investigated (Nolan and Smiles, *loc. cit.*), and it was found that a tribromo-derivative is formed, from which the dibromosulphonium-quinone may be obtained by removal of hydrogen bromide. The unstable sulphide with six atomic proportions of the halogen gave the same products. Since the present experiments with larger quantities of halogen and acetic anhydride as the solvent have yielded entirely different products, it was necessary to repeat the former experiments with glacial acetic acid, using the larger excess of halogen. However, the same results were obtained, the dibromonaphthasulphonium-quinone (Found, C=50.4, H=2.2, Br=33.6. Calc., C=50.6, H=2.1, Br=33.7 per cent.) being formed either from the quinone or from the unstable

sulphide. A correction in the melting point of this substance must be made, from the 193° formerly given to 213° obtained with a sample recrystallised from acetic anhydride. Moreover, it must also be observed that the temperature of decomposition of the tribromo-derivative, which forms the initial product of the interaction, may vary considerably according to the mode of purification, although the data of analysis remain in accord with theory. Whether this behaviour is due to the presence of slight impurities or to the presence of isomeric tribromo-derivatives is at present uncertain, but the same quinone was obtained from the many different samples examined.

Interaction of Naphthasulphonium-quinone and Acetyl Bromide.

—When the quinone is added to cold acetyl bromide it is readily attacked; the material dissolves, forming a brown solution. Further interaction does not begin until the mixture has been warmed on the water-bath, when the bromo-derivatives of naphthathioxin are gradually precipitated in the crystalline state. Heating was continued for one hour before the product was isolated by filtration from the cooled mother liquors; the yield was very poor, about 0.7 gram being obtained from every 5 grams of the quinone taken. Analysis showed that the product (m. p. 178°) consisted of monobromonaphthathioxin mixed with a small quantity of the dibromo-derivative. Attempts to obtain either substance in the pure condition were not successful, and hence for identification the substance was treated with excess of bromine in glacial acetic acid. The pure dibromo-derivative thus obtained was identical with that formed in the other various reactions described in this paper.

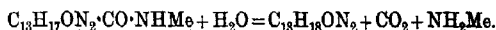
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UNIVERSITY COLLEGE, LONDON.

XLIII.—*Researches on the Constitution of Physostigmine. Part II. The Synthesis of 3-Dimethyl-aminoacetyl-2-methylindole and 2- α -Dimethyl-amino- γ -hydroxypropylindole.*

By ARTHUR HENRY SALWAY.

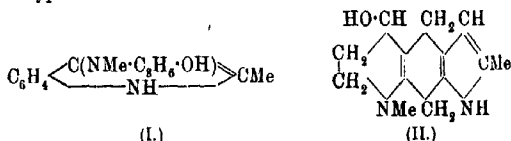
PREVIOUS investigations on the constitution of physostigmine (eserine), $C_{15}H_{21}O_2N_3$, have shown that the principal degradation product of the alkaloid is eseroline, $C_{13}H_{15}ON_2$, this substance being derived from the parent compound by alkaline hydrolysis with

elimination of carbon dioxide and methylamine, according to the equation:



The solution of the problem of the constitution of physostigmine thus depends on the determination of the constitution of eseroline. The investigation of the latter was recently undertaken by the present author (T., 1912, 101, 378), who showed that this substance is in all probability an indole derivative, since it yields 2-methylindole when distilled with zinc dust in a current of hydrogen. Moreover, it was also shown that eseroline is a tertiary monacid base containing a methyl group attached to nitrogen, that it possesses weakly acid properties, and that it rapidly absorbs oxygen in the presence of alkalis with the formation of rubreserine, eserine-blue, and other oxidation products. Whilst this knowledge concerning the properties of eseroline and its degradation products is insufficient to enable the author to propose a constitution for the alkaloid with a reasonable degree of certainty, it nevertheless seemed desirable for the purpose of the present investigation to construct a hypothetical formula which would serve as a basis for some synthetical experiments.

In the construction of such a formula it is evident that the methylindole complex, which eseroline presumably contains, will account for the group of atoms $\text{C}_6\text{H}_5\text{N}$, the nitrogen atom of which will correspond with the non-basic nitrogen atom of eseroline. The remaining part of the molecule, $\text{C}_4\text{H}_5\text{ON}$, will contain a tertiary basic nitrogen atom attached to a methyl group, and also, in all probability, a hydroxyl group,* and may therefore be further resolved into the group $\text{C}_3\text{H}_5(\text{OH})(\text{NMe})$. The nature of the union between the indole complex and the group $\text{C}_3\text{H}_5(\text{OH})(\text{NMe})$ now remains to be considered. In the first place, the latter might be in combination with the indole nucleus as an aliphatic side-chain, in which case eseroline would be represented by a formula of the type I:

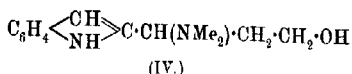
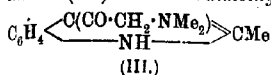


On the other hand, there exists the possibility that the group, $\text{C}_3\text{H}_5(\text{OH})(\text{NMe})$, forms a closed chain with the indolic part of the molecule. In this case the simplest formula which can be con-

* The presence of a hydroxyl group in eseroline is probable, but has not been established beyond question.

structed in agreement with the known properties of eseroline is of the type II.

The author has now undertaken the synthesis of compounds belonging to the types I and II in the hope of obtaining more definite knowledge regarding the constitution of eseroline. In the present investigation two derivatives of indole containing a basic and oxygenated side-chain, namely, 3-dimethylaminoacetyl-2-methylindole (III) and 2- α -dimethylamino- γ -hydroxypropylindole (IV),



have been prepared, and their properties compared with those of eseroline. It has been found that these synthetic compounds possess properties which differ greatly from those of eseroline, and it may therefore be concluded that the latter is not a simple substituted indole of the type represented by formula I.

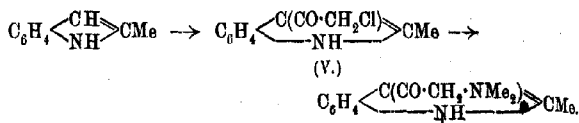
It is proposed in subsequent investigations to attempt the synthesis of compounds of the kind represented by formula II.

A number of general methods are known for the synthesis of substituted indoles, but whilst a few of these can be applied with good results in the preparation of the simpler indole derivatives, none of them appears to be of much service in the preparation of indoles with an extended side-chain. Recently, however, Oddo (*Gazzetta*, 1911, **41**, i, 234) has indicated the possibility of preparing indoles, substituted in the 3-position, by the aid of the Grignard reaction, whilst Madelung (*Ber.*, 1912, **45**, 1128, 3541) has found that *o*-toluidides may be converted into substituted indoles by heating with sodium ethoxide at a high temperature. These methods have now been used by the author for the preparation of the indole compounds described in the present investigation.

EXPERIMENTAL.

I.—Synthesis of 3-Dimethylaminoacetyl-2-methylindole (III).

Oddo has shown (*loc. cit.*) that indole reacts with magnesium methyl iodide with the formation of magnesium indolyl iodide, which by subsequent treatment with acetyl chloride yields 3-acetylindole. In the present experiments a similar process has been employed for the conversion of 2-methylindole into 3-chloroacetyl-2-methylindole, which then yielded 3-dimethylaminoacetyl-2-methylindole on treatment with dimethylamine. These changes are represented in the following scheme:



3-Chloroacetyl-2-methylindole (V).

For the preparation of this compound two parts of magnesium powder were mixed with nine parts of ethyl bromide in the presence of dry ether. After the magnesium had completely dissolved, eleven parts of 2-methylindole, dissolved in dry ether, were added drop by drop, and the mixture kept at the ordinary temperature for about an hour. Chloroacetyl chloride (nine parts), dissolved in ether, was then slowly added in the cold. At first the addition of the latter caused the precipitation of a viscid, yellow solid, which finally became cherry-red. After all the chloroacetyl chloride had been added, the upper layer of ethereal liquid was decanted, and the viscid solid which remained was agitated vigorously with an aqueous solution of sodium hydrogen carbonate, when an almost colourless solid, insoluble in the alkaline liquid, was obtained. This was collected, dried, and crystallised several times from ethyl acetate, from which it was deposited in slender, colourless needles, melting at 220°:

0.0830 gave 0.1946 CO₂ and 0.0380 H₂O. C=63.9; H=5.1.

0.1286 „ 0.0876 AgCl. Cl=16.9.

C₁₁H₁₀ONCl requires C=63.6; H=4.8; Cl=17.1 per cent.

3-Chloroacetyl-2-methylindole is sparingly soluble in ether, benzene, or chloroform, but more readily so in alcohol or ethyl acetate. Its chlorine atom is very reactive, being quickly removed when heated with alkalis, and also to some extent when heated with alcohol.

In one experiment for the preparation of the above compound magnesium methyl iodide was employed in the place of magnesium ethyl bromide with a somewhat unexpected result. The product of the reaction in this case was a mixture of two compounds in approximately equal proportions. One of these compounds was the desired 3-chloroacetyl-2-methylindole melting at 220°, whilst the other melted at 197°, and did not contain chlorine. The latter substance on analysis gave the following figures:

0.1075 gave 0.3011 CO₂ and 0.0642 H₂O. C=76.4; H=6.6.

C₁₁H₁₁ON requires C=76.3; H=6.4 per cent.

It appeared probable from this result that the compound melting at 197° possessed the constitution $\text{C}_6\text{H}_7 \left\langle \begin{array}{c} \text{CAc} \\ \text{NH} \end{array} \right\rangle \text{CMe}_3$, and had been

formed in the above reaction by the reducing action of the liberated hydriodic acid on the 3-chloroacetyl-2-methylindole. If this supposition regarding the constitution of the compound melting at 197° were correct, then the same substance should be obtained by the action of acetyl chloride on magnesium 2-methylindolyl iodide. This experiment, conducted in a manner similar to that employed in the preparation of 3-chloroacetyl-2-methylindole, yielded a product identical with the above-mentioned substance melting at 197° . The latter is therefore 3-acetyl-2-methylindole.

3-Acetyl-2-methylindole is moderately soluble in chloroform or alcohol, but only sparingly so in benzene or ether. It crystallises from hot alcohol in slender, colourless needles, and from chloroform in thin, colourless plates, melting at 197° . It does not give the pine-shaving colour reaction of indole. It yields an *oxime*, which crystallises from dilute alcohol in glistening leaflets, melting and decomposing at 199° :

0.0972 gave 0.2502 CO_2 and 0.0568 H_2O . $\text{C}=70.2$; $\text{H}=6.5$.

$\text{C}_{11}\text{H}_{12}\text{ON}_2$ requires $\text{C}=70.2$; $\text{H}=6.4$ per cent.

3-Dimethylaminoacetyl-2-methylindole (III).

As quantity of 3-chloroacetyl-2-methylindole was heated for four hours at 100° in a sealed tube with an excess of dimethylamine dissolved in alcohol. The solvent and the excess of dimethylamine were first removed in a current of steam, and the mixture then acidified with dilute hydrochloric acid, when a quantity of non-basic material remained undissolved, the latter being collected and set aside for subsequent examination. The acid liquid was now made alkaline with sodium carbonate, and the precipitated base collected, washed with water, and purified by crystallisation from alcohol. It was obtained in colourless, rhombohedral prisms, which melted at 201° . The yield of pure substance amounted to 62 per cent. of the theoretical:

0.0958 gave 0.2540 CO_2 and 0.0640 H_2O . $\text{C}=72.3$; $\text{H}=7.4$.

$\text{C}_{13}\text{H}_{16}\text{ON}_2$ requires $\text{C}=72.2$; $\text{H}=7.4$ per cent.

The non-basic by-product in the above reaction was very sparingly soluble in the usual organic solvents. It was crystallised, however, from much hot acetic acid, and then obtained in small, colourless, square prisms, which melted and decomposed at 270° :

0.1304 gave 0.3243 CO_2 and 0.0760 H_2O . $\text{C}=67.8$; $\text{H}=6.5$.

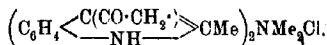
0.1980 " 0.0640 AgCl . $\text{Cl}=8.0$.

0.1718 " 14.4 c.c. N_2 at 12° and 775 mm. $\text{N}=10.2$.

$\text{C}_{21}\text{H}_{25}\text{O}_2\text{N}_3\text{Cl}$ requires $\text{C}=68.0$; $\text{H}=6.1$; $\text{N}=9.9$; $\text{Cl}=8.4$ per cent.

It appears from these results and the properties of the compound

that the latter is a quaternary ammonium salt formed by the union of one molecule of 3-dimethylaminoacetyl-2-methylindole and one of 3-chloroacetyl-2-methylindole, and therefore has the constitution:



3-Dimethylaminoacetyl-2-methylindole is sparingly soluble in ether, chloroform, or benzene, and moderately so in alcohol. It is a stable base, showing no tendency to absorb oxygen in the presence of alkalis. It does not respond to the pine-shaving test for indoles. Its *hydrochloride*, prepared by dissolving the base in dilute hydrochloric acid, evaporating the solution to dryness and crystallising the residue from alcohol, was obtained in colourless, rhombohedral crystals, melting at 258°.

Many attempts were made to reduce the above base in order to obtain from it by the addition of two atoms of hydrogen a substance of the same empirical formula as eseroline, but reduction could not be effected; thus, when the base was heated with tin and hydrochloric acid, or with sodium in amyl alcohol, no change occurred, whilst treatment with hydriodic acid and red phosphorus at 120° caused disruption of the molecule with formation of 2-methylindole.

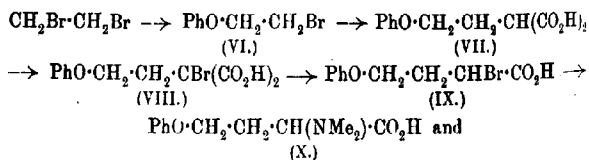
II.—Synthesis of 2- α -Dimethylamino- γ -hydroxypropylindole (IV).

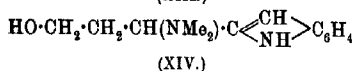
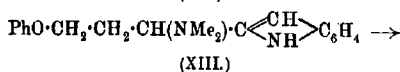
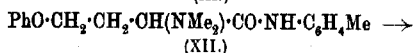
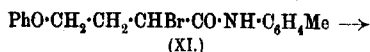
As already indicated, Madelung (*loc. cit.*) has shown that *o*-toluidides may be converted into substituted indole derivatives by heating with sodium ethoxide. Although this reaction has hitherto only been applied to the *o*-toluidides of acetic, benzoic, and oxalic acids, it appeared probable that the method might be extended to the preparation of any indole derivative, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH} \\ \text{NH} \end{array} \gg \text{CR}$, provided

that the acid $\text{R}\cdot\text{CO}_2\text{H}$ could be obtained. For the purpose of the present synthesis the radicle R was required to consist of an oxygenated acyl group containing a tertiary basic nitrogen atom, and the corresponding acid, $\text{R}\cdot\text{CO}_2\text{H}$, chosen as best fitted to meet these requirements, was α -dimethylamino- γ -hydroxybutyric acid,



The steps which were necessary for the preparation of this compound and for its conversion into the desired indole derivative are as follows:





The compounds represented by the formulæ (VI) and (VII) in the above scheme have already been described by Perkin, Bentley, and Haworth (T., 1896, 69, 169), whilst the compounds (VIII) and (IX) have been synthesised by Fischer (*Ber.*, 1907, 40, 106).

α-Dimethylamino-γ-phenoxybutyric Acid (X).

For the preparation of this compound one part of *α*-bromo-*γ*-phenoxybutyric acid, obtained from ethylene dibromide as described by the above-mentioned investigators (*loc. cit.*), was heated in a sealed tube for six hours at 100° with two parts of an aqueous solution (33 per cent.) of dimethylamine. The product was then distilled in a current of steam with a known amount of sodium hydroxide until the excess of dimethylamine had been removed. A quantity of hydrobromic acid equivalent in amount to the sodium hydroxide employed was then added, and the liquid concentrated to dryness under diminished pressure. The residue was then digested with absolute alcohol, the alcoholic liquid filtered to remove the sodium bromide, and the filtrate evaporated. The amino-acid was thus obtained as a viscid oil, which did not crystallise on keeping. When agitated with a little aqueous hydrobromic acid, however, it immediately solidified, with the formation of a crystalline hydrobromide. This was purified by recrystallisation from water, and was then obtained in colourless, thin plates, melting at 86°:

0.1183 (air-dried), heated at 110°, lost 0.0124 H₂O. H₂O=10.5.

0.1445 „ gave 0.0784 AgBr. Br=23.1.

C₁₂H₁₈O₃NBr·2H₂O requires H₂O=10.6; Br=23.5 per cent.

0.1059 * gave 0.1824 CO₂ and 0.0562 H₂O. C=47.0; H=5.9.

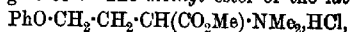
C₁₂H₁₈O₃NBr requires C=47.4; H=5.9 per cent.

In order to obtain the free base, the above-described hydrobromide was dissolved in water, and an amount of sodium carbonate added just sufficient to combine with the hydrobromic acid. The mixture was then evaporated to dryness under diminished pressure,

* Anhydrous substance.]

and the amino-acid extracted from the residue by means of absolute alcohol. After evaporating the alcoholic extract, the amino-acid was obtained as a very hygroscopic, amorphous solid, which could not be obtained crystalline.

α-Dimethylamino-*γ*-phenoxybutyric acid (X) is readily soluble in alcohol or water, insoluble in ether, benzene, or chloroform. It yields a *hydrochloride*, which crystallises from water in prismatic needles melting at 83°. The *methyl* ester of the latter,



crystallises from hot ethyl acetate in colourless aggregates of flat plates, which melt at 130°:

0.1000 gave 0.2086 CO₂ and 0.0666 H₂O. C=56.9; H=7.4.

C₁₃H₁₉O₃N.HCl requires C=57.0; H=7.3 per cent.

For the next stage in the synthesis it was necessary to prepare the *o*-toluidide of the above-described amino-acid (XII). Attempts were first made to obtain this compound from the acid chloride, PhO·CH₂·CH₂·CH(NMe₂)·COCl, but the latter could not be prepared. Ultimately the difficulty was overcome by first preparing the *o*-toluidide of *α*-bromo-*γ*-phenoxybutyric acid (XI), and subsequently displacing the bromine in this compound by the dimethylamino-group.

α-Bromo-*γ*-phenoxybutyro-*o*-toluidide (XI).

Seven parts of *α*-bromo-*γ*-phenoxybutyric acid were dissolved in ether, and six parts of phosphorus pentachloride added. After the reaction had subsided, the ether, together with the phosphoryl chloride which had been formed, was removed on the water-bath under diminished pressure, and the residual crude acid chloride then added to an excess of *o*-toluidine dissolved in ether. A voluminous precipitate of the *o*-toluidide was thus formed, which was collected, washed with water, and recrystallised from hot alcohol, when it separated in colourless, prismatic needles, melting at 147°:

0.1000 gave 0.2145 CO₂ and 0.0478 H₂O. C=58.5; H=5.3.

C₁₇H₁₈O₂NBr requires C=58.6; H=5.2 per cent.

α-Bromo-*γ*-phenoxybutyro-*o*-toluidide is only moderately soluble in ether, but more readily so in chloroform, ethyl acetate, or alcohol.

α-Dimethylamino-*γ*-phenoxybutyro-*o*-toluidide (XII).

This substance was prepared by heating the foregoing compound in a sealed tube at 100° for two hours with an excess of dimethylamine dissolved in alcohol. The alcohol and excess of dimethylamine were then removed in a current of steam, when the required

base was precipitated as a colourless oil. This was dissolved in ether, the ethereal solution dried, and the solvent removed. The residual oil slowly solidified, and was then purified by crystallisation from light petroleum, when it separated in radiating clusters of colourless, prismatic needles, melting at 54° :

0.1265 gave 0.3376 CO_2 and 0.0898 H_2O . $\text{C}=72.8$; $\text{H}=7.9$.

$\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_2$ requires $\text{C}=73.1$; $\text{H}=7.7$ per cent.

α -Dimethylamino- γ -phenoxybutyro-*o*-toluidide is very readily soluble in the usual organic solvents, and can only be crystallised with difficulty. It is a weak base, forming salts which are acid towards litmus, and also possess an extremely bitter taste. The hydrochloride, prepared by passing a current of dry hydrogen chloride into an ethereal solution of the base, crystallises from a mixture of alcohol and ethyl acetate in slender, colourless needles, melting at 169° :

0.1010 gave 0.2410 CO_2 and 0.0646 H_2O . $\text{C}=65.1$; $\text{H}=7.1$.

$\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_2\cdot\text{HCl}$ requires $\text{C}=65.4$; $\text{H}=7.2$ per cent.

The platinichloride of the above base crystallises from alcohol, containing a little hydrochloric acid, in small, brown prisms, melting at 215° .

2- α -Dimethylamino- γ -hydroxypropylindole.

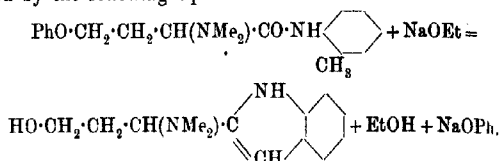
In order to prepare this compound 0.3 gram of sodium was dissolved in absolute alcohol in a capacious flask, and the alcohol removed under diminished pressure; to the sodium ethoxide thus obtained, 2 grams of α -dimethylamino- γ -phenoxybutyro-*o*-toluidide were added, and the mixture heated in a metal bath to a temperature of 250 – 300° in a current of hydrogen. At this temperature reaction took place with effervescence and a considerable darkening in colour, and the process was soon complete. The entire operation was repeated four times with the same quantities of material, and the products from the several reactions were then united and acidified with dilute hydrochloric acid. The acid liquid was next shaken with ether, which removed a considerable quantity of phenol, identified by means of its tribromo-derivative, then made alkaline with sodium carbonate, and the mixture repeatedly extracted with chloroform. The chloroform extracts were washed, dried, and the solvent removed, when an oily, basic residue was obtained, which did not crystallise on keeping. For its purification it was dissolved in dilute hydrochloric acid, the solution evaporated to dryness under diminished pressure, and the solid residue thus obtained crystallised from a mixture of alcohol and ethyl acetate. The hydrochloride of the base then separated in colourless, prismatic

needles, melting at 218°. The amount of pure hydrochloride obtained from 10 grams of the *o*-toluidide was 3.3 grams:

0.0962 gave 0.2166 CO₂ and 0.0646 H₂O. C=61.4; H=7.5.

C₁₃H₁₈ON₂·HCl requires C=61.3; H=7.5 per cent.

It is evident from this result that the sodium ethoxide in the above reaction has not only effected the expected indolic condensation, but has also simultaneously removed the phenyl group with the formation of 2- α -dimethylamino- γ -hydroxypropylindole, as represented by the following equation:



2- α -Dimethylamino- γ -hydroxypropylindole.—The pure base was prepared from the above-described hydrochloride by treating the latter with aqueous sodium carbonate, and extracting the alkaline liquid with chloroform; after the removal of the chloroform, the base was obtained as a colourless, volatile oil, which did not solidify in a freezing mixture. It was miscible with ether, chloroform, ethyl acetate, alcohol, or water:

0.0910 gave 0.2375 CO₂ and 0.0698 H₂O. C=71.2; H=8.5.

C₁₃H₁₈ON₂ requires C=71.6; H=8.3 per cent.

The *aurichloride* of the above base crystallises from dilute alcohol in yellow prisms, which melt at 133° and are anhydrous:

0.1140 gave 0.1174 CO₂, 0.0353 H₂O, and 0.0400 Au. C=28.1;

H=3.4; Au=35.1.

C₁₃H₁₈ON₂·HAuCl₄ requires C=28.0; H=3.4; Au=35.3 per cent.

The *picrate* crystallises from dilute alcohol in spherical aggregates of bright yellow rhombs, which melt at 140°.

The base, 2- α -dimethylamino- γ -hydroxypropylindole, which has now been synthesised, is isomeric with the alkaloid eseroline. The properties of these two compounds are, however, very dissimilar, as a comparison shows: thus, eseroline in the presence of alkalis readily absorbs oxygen with the production of intensely coloured solutions, whilst the synthetic base is quite stable under similar conditions. Moreover, eseroline readily reduces gold and silver salts, and is also a strong base, which yields neutral salts. The synthetic base, on the other hand, possesses no reducing properties, and is a weak base yielding salts with a strongly acid reaction. The synthetic base, furthermore, differs considerably from eseroline in physiological action, as shown by some experiments kindly conducted by Dr.

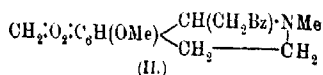
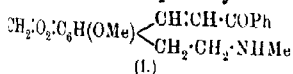
H. H. Dale, director of the Wellcome Physiological Research Laboratories, to whom the author here wishes to express his best thanks: thus, on the one hand, eseroline was found to produce the characteristic myotic action of physostigmine (but in a diminished degree) when injected into the eye, and also to effect a slowing of the heart-beat after intravenous injection. The synthetic base, 1- α -dimethylamino- γ -hydroxypropylindole, on the other hand, possessed none of these physiological properties.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

XLIV.—*Synthetical Experiments in the Group of the isoquinoline Alkaloids. Part III. The Constitution of Anhydrocotarnineacetophenone, etc., together with an Account of Some New Condensation Products of Cotarnine.*

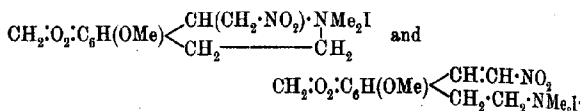
By EDWARD HOPE and ROBERT ROBINSON.

At an early stage of this series of experiments (Part I, T., 1911, 99, 1153; Part II, *ibid.*, 2114) it became evident that certain statements made by Liebermann and his co-workers with regard to the constitution of the condensation products of cotarnine with various substances were without satisfactory experimental foundation (Liebermann and Kropf, *Ber.*, 1904, 37, 211; Liebermann and Glawe, *ibid.*, 2738; Kropf, *ibid.*, 2744). In the light of the explanation of the ready condensation of cotarnine with various nitro-compounds (T., *loc. cit.*, 2117), and, indeed, with a number of substances containing reactive hydrogen atoms, we have repeated some of these earlier experiments, and have examined particularly the cases of condensation with acetophenone and ethyl phenylacetate. Liebermann and Glawe recognised the possibility of two structures for the condensation products of cotarnine. Anhydrocotarnineacetophenone might be represented by (I) or (II), a derivative of *N*-methylaminoethylbenzaldehyde, or of *N*-methyltetrahydroisoquinoline respectively:

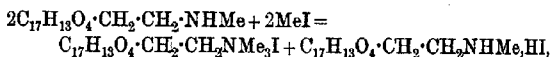


In this connexion Liebermann and Glawe say: "It is possible to discriminate between the two forms in various ways, especially by proving the presence of a hydrogen atom attached to nitrogen by methylation or acylation." Using such methods, they concluded that some condensation products had the structure corresponding with (I)—and here were classed all the condensation products of cotarnine with "active" methylene groups—whilst others had the structure (II).

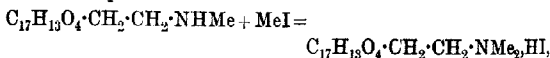
If the above-mentioned methods were universally trustworthy, there would be little difficulty in determining the constitution of any of the condensation products in question. The present authors have, however, already described (T., 1911, 99, 2120) the remarkable formation of a mixture of methiodides from anhydrocotarnine-nitromethane (a perfectly homogeneous substance which possesses the tetrahydroisoquinoline structure). These methiodides agree in properties and composition with the formulæ:



and it therefore appears that methyl iodide may cause the partial transformation of the cyclic form of anhydrocotarninenitromethane into the open-chain form. A substance exhibiting similar properties to anhydrocotarninenitromethane is anhydrocotarnineacetophenone. It was observed by Kropf that the behaviour of this compound with methyl iodide varied with the experimental conditions, particularly the temperature; but these reactions were explained in accordance with the open-chain formula as follows: The reaction with methyl iodide in the cold (or in methyl-alcoholic solution) was supposed to occur thus:



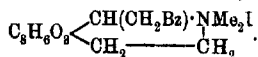
whilst if the reaction was allowed to proceed without cooling, its course was represented thus:



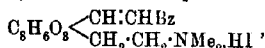
the sole product in this case being the hydriodide of methyl-anhydrocotarnineacetophenone.

Our experimental results agree in the main with those of Kropf, but we put forward the following interpretation, which we believe to be more satisfactory than that summarised above. Anhydrocotarnineacetophenone has the tetrahydroisoquinoline structure (II, p. 361), but is capable of reacting in the tautomeric form with

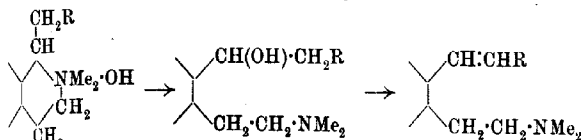
reagents like benzoyl chloride and methyl iodide. When methyl iodide alone reacts with anhydrocotarnineacetophenone and the interaction is allowed to proceed without cooling, the cyclic structure remains intact and the methiodide,



melting at 180° , is produced. Kropf regarded this as the hydriodide of methylanhydrocotarnineacetophenone:



but the preparation of the latter by the action of hydriodic acid on methylanhydrocotarnineacetophenone showed the two substances to be totally different. Kropf's principal reason for believing this substance to be a hydriodide was that its aqueous solution gave an immediate precipitate of methylanhydrocotarnineacetophenone when treated with alkalis. This we regard as nothing more than the usual change which occurs when all similar derivatives of the quaternary ammonium salts of tetrahydroisoquinoline are treated with sodium hydroxide and potassium hydroxide:

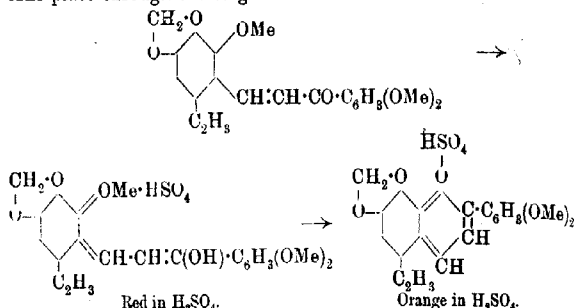


Further, although, as mentioned above, anhydrocotarnineacetophenone yields a benzoyl derivative, it does not do so smoothly, and the difficulty of obtaining this derivative in good yield is very considerable. It is therefore believed that benzoyl chloride behaves like methyl iodide in causing the scission of the hydrocotarnine ring.

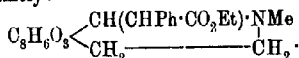
It is not easy to determine whether a minute amount of the open-chain form of anhydrocotarnineacetophenone exists in equilibrium with the cyclic form. If this be so, benzoyl chloride, which reacts only with the open-chain form, will progressively change the whole of the substance into this form, whilst methyl iodide, which reacts with both of the possible forms of anhydrocotarnineacetophenone, will only cause the conversion of a portion of this substance into the open-chain form. It is hoped to throw some light on this matter by the spectroscopic examination of a number of derivatives of substances allied in constitution to anhydrocotarnineacetophenone.

In connexion with the degradation of anhydrocotarnineacetophenone to cotarnonideneacetophenone by the Hofmann process, we

found it necessary to synthesise the latter from cotarnone and acetophenone. The similarly constituted substance obtained from resacetophenonedimethyl ether exhibited an interesting behaviour on treatment with concentrated sulphuric acid. It dissolves in this reagent with the production of a red colour, which, however, quickly changes to orange. When the orange solution is poured into water, a solution of an oxonium salt is produced, as evidenced by the formation of a picrate and a platinichloride. These changes take place through the stages:

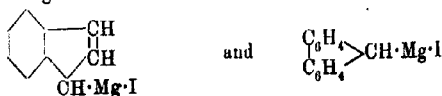


A complete examination of ethyl anhydrocotarninephenylacetate showed that it was constituted analogously to anhydrocotarnineacetophenone, namely:

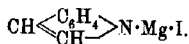


The cyclic structure is, however, vastly more stable. No trace of a benzoyl derivative could be obtained by vigorous treatment with benzoyl chloride, nor could a nitroso-compound be prepared.

At the end of the experimental portion of this paper are described some new condensation products of cotarnine with substances containing active hydrogen atoms, namely, 1-hydrindone, 1:3-diketohydrindene, indene, fluorene, isatin, and α -methylindole. Although the constitutional formulæ assigned to these substances have not as yet been experimentally founded, there can be little doubt regarding the correctness of the structure given in the experimental portion of the paper. The active hydrogen in some of the above-mentioned substances has been located by means of magnesium methyl iodide; for example, indene and fluorene yield one molecule of methane in each case, forming magnesium derivatives having the constitutions:



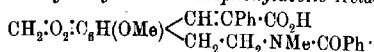
respectively. In the case of α -methylindole it is highly probable that the most reactive hydrogen atom is that attached to the nitrogen, as in indole itself, Oddo (*Gazzetta*, 1911, **41**, i, 221) having shown that the product of the interaction of the latter with magnesium methyl iodide possesses the constitution:



It is a curious fact that it has so far been found impossible to condense cotarnine with diphenylamine or carbazole, although these compounds show the presence of active hydrogen by their behaviour towards Grignard reagents, as well as by their formation of potassium compounds.

EXPERIMENTAL.

Benzoylanhydrocotarninephenylacetic Acid,



This acid was prepared in order to obtain evidence bearing on the constitution of ethyl anhydrocotarninephenylacetate. A mixture of benzoylcotarnine (13 grams), sodium phenylacetate (16 grams), and acetic anhydride (26 grams) was heated at 130–135° (temperature regulated) for three days.

The product was poured into hot water and washed with several changes to remove acetic anhydride and sodium acetate. The oil was then shaken with sodium carbonate and ether, and the aqueous layer separated and acidified with concentrated hydrochloric acid. The yellow precipitate was collected and crystallised from aqueous alcohol. It was obtained in small, colourless, lozenge-shaped plates, melting at 205–206°, which were dried in a vacuum over sulphuric acid:

0.1263 gave 0.3262 CO_2 and 0.0592 H_2O . $\text{C} = 70.4$; $\text{H} = 5.2$.

0.2587 „ 7.5 c.c. N_2 at 22° and 764 mm. $\text{N} = 3.3$.

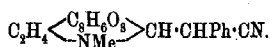
$\text{C}_{27}\text{H}_{25}\text{O}_6\text{N}$ requires $\text{C} = 70.6$; $\text{H} = 5.4$; $\text{N} = 3.1$ per cent.

This acid is of remarkable stability, and although many attempts were made to hydrolyse it they were quite fruitless, since the acid was usually recovered unchanged. Unlike most substances derived from cotarnine this acid can be heated to 280° without decomposition. The double linking appears to be sterically affected, since a solution of the acid in sodium carbonate does not decolorise potassium permanganate in the cold, nor does the substance take up bromine with any readiness (compare p. 369).

Since we were unable to hydrolyse the benzoyl compound we attempted to benzoylate ethyl anhydrocotarnine phenylacetate, but

this substance behaves differently from anhydrocotarnineacetophenone (see p. 369), and no trace of a benzoyl derivative could be isolated.

Anhydrocotarninephenylacetonitrile,



A solution of cotarnine (10 grams) and phenylacetonitrile (5 grams) in methyl alcohol (20 c.c.) was allowed to remain at the room temperature. The condensation product, which separated after half an hour, was collected, washed with methyl alcohol, and crystallised from ethyl acetate. The substance occurs in large, colourless prisms, readily soluble in hot ethyl acetate, but sparingly so in methyl or ethyl alcohols. It begins to decompose at 135° , and melts to a red liquid at 153 – 155° :

0.1467 gave 0.3859 CO_2 and 0.0800 H_2O . $\text{C}=71.7$; $\text{H}=6.0$.

$\text{C}_{20}\text{H}_{20}\text{O}_3\text{N}_2$ requires $\text{C}=71.4$; $\text{H}=5.9$ per cent.

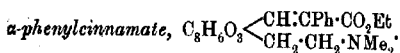
The formation of the red substance, obtained when the compound is fused, is also observed when the solution of the nitrile in solvents of high boiling point, for example, xylene, are boiled, and this reaction is highly characteristic.

The substance shows the usual reactions associated with its basic character, and is decomposed by hot acetic acid, with the production of cotarnine and phenylacetonitrile.

Methylanhydrocotarninephenylacetonitrile Picrate.—Anhydrocotarninephenylacetonitrile was mixed with methyl sulphate, when reaction occurred with evolution of heat, and the product was a colourless, crystalline methosulphate, which was dissolved in hot water and treated with excess of sodium hydroxide. The resulting colourless oil could not be solidified, and was therefore dissolved in ether, and, after evaporation of the dried ethereal solution, dissolved in alcohol and mixed with an alcoholic solution of picric acid. The *picrate* of the base separated in bright yellow prisms, and was recrystallised from ethyl alcohol, in which it is sparingly soluble in the cold. The crystals are clusters of prismatic needles of highly characteristic shape, and melt at 169 – 170° without decomposition:

0.1525 gave 16.0 c.c. N_2 at 13° and 758 mm. $\text{N}=12.4$.

$\text{C}_{21}\text{H}_{22}\text{O}_3\text{N}_2 \cdot \text{C}_6\text{H}_3\text{O}_3\text{N}_3$ requires $\text{N}=12.1$ per cent.

Ethyl 2-Methoxy-3:4-methylenedioxy-6-β-dimethylaminoethyl-

In preparing ethyl anhydrocotarninephenylacetate * Liebermann and Glawe (*Ber.*, 1904, **37**, 2738) employed sodium carbonate as condensing agent, but we have found that a good yield may be obtained by simply mixing cotarnine with ethyl phenylacetate in molecular quantities in cold alcohol. The ester was heated on the steam-bath with an excess of methyl iodide, and in the course of about fifteen minutes the contents of the flask became quite solid owing to the separation of the methiodide. The excess of methyl iodide was removed by distillation, and the residue crystallised from alcohol. Six grams of the pure substance are obtained from 5 of the ester. The compound forms long, faintly yellow prisms, melting at 173—174°:

0.1151 gave 0.2203 CO_2 and 0.0605 H_2O . $C = 52.2$; $H = 5.8$.

0.1112 „ 0.0493 AgI . $I = 24.0$.

$C_{23}H_{28}O_6NI$ requires $C = 52.6$; $H = 5.4$; $I = 24.0$ per cent.

The methiodide (2.6 grams) was dissolved in a little hot water, and warmed on the steam-bath with precipitated silver chloride (1 gram) for three-quarters of an hour. The silver iodide was then separated by filtration from the aqueous solution of the methochloride, to which *N*-sodium hydroxide (7 c.c.) was added. The precipitated oil was extracted with ether, the ethereal solution dried, and distilled, leaving an uncrystallisable residue. The substance was, however, obtained in a sufficiently pure condition for analysis by dissolving the oil in dilute hydrochloric acid and extracting the basified solution with ether. The viscid oil remain-

* It is curious that two substances have been isolated by crystallisation of the picrates of both ethyl anhydrocotarninephenylacetate and its methohydroxide.

Ethyl Anhydrocotarninephenylacetate Picrates.

The mixture of substances is obtained as a yellow precipitate when picric acid is added to a solution of the substance in dilute hydrochloric acid. On crystallisation from methyl alcohol the first fraction consists of hexagonal plates melting at 124—126°, and is produced in considerable quantity, whilst the second fraction is obtained in long rods which melt at 138—142°.

Ethyl anhydrocotarninephenylacetate methohydroxide picrates are obtained by the addition of aqueous picric acid to a solution of the corresponding methiodide. On fractional crystallisation from methyl alcohol the first crop consists of plates and melts at 119—120°, whilst the second and larger fraction also crystallises in plates, differs characteristically in that crystals evolve solvent on crystallisation at 110—114°, resolidify, and then melt at 162—163°. We have not yet accumulated sufficient data to enable us to determine the nature of these substances.

ing after evaporation of the ether and long exposure to a vacuum was analysed:

0.1582 gave 0.3977 CO_2 and 0.0958 H_2O . $\text{C}=68.5$; $\text{H}=6.7$.

$\text{C}_{23}\text{H}_{27}\text{O}_5\text{N}$ requires $\text{C}=69.5$; $\text{H}=6.8$ per cent.

The agreement is as close as can be expected for an uncrystallised substance.

The colourless solution of the base in concentrated hydrochloric acid gives, on the addition of water, a precipitate which redissolves in excess.

The Picrate.—The solution of the base in dilute acid was treated with aqueous picric acid, when a bright yellow picrate was obtained, and after separation the derivative was crystallised from methyl alcohol. It was so obtained in magnificent, yellow prisms, melting at $195-196^\circ$:

0.2100 gave 0.4256 CO_2 and 0.0923 H_2O . $\text{C}=55.3$; $\text{H}=4.8$.

$\text{C}_{23}\text{H}_{27}\text{O}_5\text{N}, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires $\text{C}=55.6$; $\text{H}=4.8$ per cent.

The Platinichloride.—When platinic chloride is added to a solution of the base in dilute hydrochloric acid, an almost colourless precipitate is obtained. The substance was purified to a certain extent by boiling with a large quantity of water, and after drying melted at $208-209^\circ$:

0.1171 gave 0.0189 Pt. $\text{Pt}=16.1$.

$(\text{C}_{23}\text{H}_{27}\text{O}_5\text{N})_2\text{H}_2\text{PtCl}_6$ requires $\text{Pt}=16.2$ per cent.

The Methiodide.—An excess of methyl iodide was poured on the oily base, when a vigorous reaction took place almost immediately; the temperature reached the boiling point of methyl iodide in a few seconds, and a crystalline solid was produced. After stirring the mixture, the excess of methyl iodide was evaporated, and the residue, a white solid, crystallised from methyl alcohol. The glistening, colourless prisms which separated melted at 197° with some change at 183° , probably evolution of solvent of crystallisation:

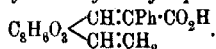
0.1690 gave 0.3278 CO_2 and 0.0829 H_2O . $\text{C}=52.9$; $\text{H}=5.4$.

0.1345 „ 0.0546 AgI. $\text{I}=21.9$.

$\text{C}_{24}\text{H}_{30}\text{O}_5\text{NI}, \text{CH}_3\text{I}$ requires $\text{C}=52.6$; $\text{H}=5.9$; $\text{I}=22.1$ per cent.

There can be no doubt that the substance contains one molecule of methyl alcohol of crystallisation.

2-Methoxy-3:4-methylenedioxy-6-vinyl- α -phenylcinnamic Acid,



The methiodide (8 grams), just described, was converted into methochloride by heating with silver chloride (6 grams) in aqueous

solution. After filtration the solution was treated with potassium hydroxide (8 c.c. of 40 per cent. aqueous solution), and boiled until the evolution of trimethylamine ceased. On cooling the liquid a sparingly soluble potassium salt separated, and this was purified by recrystallisation from water. The pure potassium salt was dissolved in water, and acidified with hydrochloric acid, when a colourless precipitate was obtained, which was collected, washed with water, and dried:

0.1240 gave 0.3188 CO_2 and 0.0595 H_2O . $\text{C}=70.1$; $\text{H}=5.3$.

$\text{C}_{19}\text{H}_{16}\text{O}_5$ requires $\text{C}=70.4$; $\text{H}=4.9$ per cent.

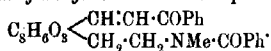
The acid could not be crystallised, but when prepared very carefully in the manner described above was found to melt at $144-146^\circ$. It is of interest that this doubly unsaturated substance only combines with two atoms of bromine:

0.9430 absorbed in chloroform solution 0.48 Br.

This weight of a substance, $\text{C}_{19}\text{H}_{16}\text{O}_5$ (absorbing two atoms of Br), would require 0.47 Br.

Clearly the vinyl group has been saturated, but, as in the case of benzoylanhydrocotarninephenylacetic acid (see p. 365), the second ethylenic linking is protected by the heavy groups which surround it. The dibromo-acid remaining in the chloroform could not be isolated in a pure condition.

Benzoylanhydrocotarnineacetophenone,



The condensation of cotarnine and acetophenone has been effected by Liebermann and Kropf (*Ber.*, 1904, **37**, 211), but the sodium carbonate, recommended by these authors as a condensing agent, is unnecessary, since under the following conditions an almost theoretical yield of pure substance may be obtained.

Cotarnine (31.6 grams) and acetophenone (16 grams) were dissolved in methyl alcohol (40 c.c.), and the solution allowed to remain at the room temperature for six hours. The introduction of a small crystal of the condensation product, or scratching of the walls of the vessel, now caused a plentiful crystallisation, and the product after collection weighed 43.5 grams. A further small quantity was recovered from the mother liquor. Kropf (*Ber.*, 1904, **37**, 2744) subjected this condensation product to the action of benzoyl chloride and aqueous potassium hydroxide, and obtained a benzoyl derivative, to which he ascribed the melting point $107-108^\circ$. In repeating this process we have obtained, although in poor yield, a compound melting at $131-132^\circ$, and this is

undoubtedly anhydrobenzoylcotarnineacetophenone, since the same substance may also be obtained by the following method: Benzoylcotarnine (2.5 grams) and acetophenone (1.1 grams) were dissolved in ethyl alcohol (20 c.c.) mixed with aqueous potassium hydroxide (0.3 c.c. of 50 per cent.), and the solution gently heated on the steam-bath during twenty-four hours. The product separated on cooling, and was purified by crystallisation from methyl alcohol, or from a mixture of benzene and light petroleum:

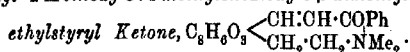
0.1754 gave 0.4710 CO_2 and 0.0946 H_2O . $\text{C}=73.2$; $\text{H}=5.9$.

0.1616 „ 4.35 c.c. N_2 at 18° and 760 mm. $\text{N}=3.1$.

$\text{C}_{27}\text{H}_{25}\text{O}_5\text{N}$ requires $\text{C}=73.1$; $\text{H}=5.6$; $\text{N}=3.2$ per cent.

This substance crystallises in characteristic, greenish-yellow tufts of needles melting at 131 – 132° , and yields in sulphuric acid an intensely red solution. The process described above results in a very good yield of the substance, but the amount of potassium hydroxide cannot be varied very much. With less the condensation is too slow, whilst if more is employed a precipitate of potassium benzoate is produced. The identity of the substance with that obtained by the benzylation of anhydrocotarnineacetophenone was proved by the fact that a mixture of the two substances melted sharply at 131 – 132° . It is interesting to note that benzoylcotarnine does not condense *per se* with ketones, etc., but is similar in its reactions to cotarnone and other aromatic aldehydes.

Phenyl 2-Methoxy-3:4-methylenedioxy-6-β-dimethylamino-



The action of methyl iodide on anhydrocotarnineacetophenone was investigated by Kropf (*loc. cit.*), who states that the main product obtained when the reaction is conducted in methyl-alcoholic solution is a methyl methiodide of the base, whilst with an excess of the methyl iodide alone the hydriodide of methylanhydrocotarnineacetophenone is produced. We have confirmed the first part of this statement, but regard the production of a dimethyl iodide as another example of the opening of the hydrocotarnine ring, so that the action of methyl iodide on anhydrocotarnineacetophenone resembles that of the same reagent on anhydrocotarninenitromethane (Hope and Robinson, T., 1911, 99, 2120). On the other hand, we believe that Kropf's methylanhydrocotarnineacetophenone hydriodide is in reality a normal methiodide of anhydrocotarnineacetophenone, and experimental evidence in favour of this view is given below. Although the nature of the products of the action of methyl iodide on the base varies according to the conditions of the reaction, this is not the case with methyl sulphate,

and a straightforward methylation without secondary products was achieved.

Anhydrocotarnineacetophenone Methosulphate.

Anhydrocotarnineacetophenone dissolved in warm benzene was treated with pure methyl sulphate (1.5 mol.), when in a short time the additive compound crystallised from the solution in theoretical amount. It was collected, washed with light petroleum, and crystallised from methyl alcohol. Large, colourless prisms were obtained, melting at 195–200° without decomposition.

The substance is readily soluble in hot methyl alcohol, sparingly so in the cold solvent.

When treated in aqueous solution with potassium iodide, anhydrocotarnineacetophenone methiodide is obtained. This substance crystallises from methyl alcohol in diamond-shaped prisms, and is identical in every way with the product of the action of methyl iodide on anhydrocotarnineacetophenone. It melts at 180° with very little decomposition. (Kropf, *loc. cit.*, gives 171° as the melting point of his methylanhydrocotarnineacetophenone hydr. iodide.)

The base figured at the head of this section (compare Kropf, *loc. cit.*) was prepared in the following manner: A solution of the above methosulphate (10 grams) in warm water (500 c.c.) was covered with an equal volume of light petroleum (b. p. 50–60°), and rendered strongly alkaline by means of potassium hydroxide. The colourless precipitate at first produced does not dissolve in the petroleum, and probably consists of the ammonium hydroxide, which, however, quickly decomposes, and yields a yellow substance which is completely extracted by the petroleum. The extract was dried with potassium carbonate, and after concentration deposited a mass of yellow, prismatic needles, melting after recrystallisation at 74–75°. (Found, C=71.4; H=6.6. Calc., C=71.4; H=6.5 per cent.)

Kropf (*loc. cit.*) assigned the melting point 78° to this substance, which he obtained by the action of alkali on anhydrocotarnineacetophenone methiodide.

The Hydriodide.—This derivative is of interest, since we have found by direct comparison that it is quite different from the methiodide of anhydrocotarnineacetophenone, which latter must, therefore, have a hydrocotarnine structure. It was obtained by the addition of potassium iodide to a solution of the above methyl base in dilute sulphuric acid. It crystallises from methyl alcohol, in which it is very readily soluble, in rectangular prisms containing solvent of crystallisation. This is lost at 100°, and the yellow powder then melts at about 156°. It differs from the isomeric

methiodide markedly in combining both with water and methyl alcohol of crystallisation.

The *perchlorate* crystallises from methyl alcohol in pale yellow, slender needles, melting at 133—135°. It is very sparingly soluble in hot water.

The *picrate* is prepared by mixing hot acetone solutions of picric acid and the base. It crystallises from acetone in large, orange prisms, is sparingly soluble, and melts at 196°.

The *ferrichloride* prepared in the usual way crystallises from acetic acid in compact, reddish-brown prisms, melting at 176°.

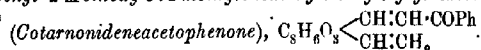
The *Methosulphate*.—This compound was prepared from its components exactly as in the case of anhydrocotarnineacetophenone methosulphate (see above). The product was crystallised from methyl alcohol, and obtained in yellow needles, which soften at 205°, and melt and decompose at 236°. Its solutions in water and methyl alcohol are intensely yellow:

0.1166 gave 0.0566 BaSO₄. S=6.7.

C₂₃H₂₉O₈NS requires S=6.6 per cent.

The *Methiodide*.—The purest specimens of this derivative were obtained by the action of potassium iodide on the above methosulphate in aqueous solution. The product was crystallised from methyl alcohol, and obtained in pale yellow prisms melting at 238—239°. The same substance is produced by the direct addition of methyl iodide to the methyl base, and also by the action of methyl iodide on anhydrocotarnineacetophenone under the conditions described by Kropf (*loc. cit.*). Prolonged recrystallisation of these products raises their melting points to 238—239° (Kropf gives 226°).

Phenyl 2-Methoxy-3:4-methylenedioxy-6-vinylstyryl Ketone



The methiodide (5 grams) described at the end of the last section was dissolved in the least possible amount of hot water, and treated with silver chloride (4 grams) so as to obtain the more soluble methochloride. The filtered liquid was cooled to 50°, and mixed with 10 c.c. of *N*-sodium hydroxide solution, and allowed to remain during twenty-four hours. The yellow solution had a strong odour of acetophenone and trimethylamine, and after filtration was rapidly distilled, the flask being immersed in an oil-bath. The distillate contained trimethylamine (platinichloride, m. p. 238°) and acetophenone (piperonylidene derivative, m. p. 122°). The distillation was stopped when the liquid had reached one-third of its original volume, and the evaporation was continued on the

steam-bath. The residue was treated with dilute hydrochloric acid, the solid separated and crystallised from methyl alcohol, and then again from ethyl alcohol. It was so obtained in pale yellow, prismatic crystals melting at 103° , this value being unaltered by admixture of the substance with an equal quantity of cotarnonideneacetophenone prepared as described below. The methyl-alcoholic mother liquor was diluted with an equal volume of water, the solution warmed with animal charcoal, cooled, filtered, and extracted with ether. The ethereal solution was dried, and evaporated nearly to dryness, when a small quantity of crystals melting at 78° was obtained. The substance was thus identified as cotarnone, and this was confirmed by the preparation of the condensation product with 2:4-dinitrotoluene, which melts at 163° (Hope and Robinson, T., 1911, 99, 2131).

Synthesis of Cotarnonideneacetophenone.

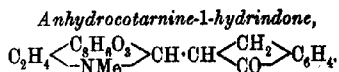
Cotarnone (3 grams) and acetophenone (3 grams) were dissolved in methyl alcohol (30 c.c.) and heated on the steam-bath for ten minutes with potassium hydroxide (6 c.c. of 30 per cent. aqueous solution). On cooling an oil separated, which became partly solid after scratching the sides of the containing vessel. The substance was collected, and thoroughly freed from oily impurities by contact with porous porcelain. It was then crystallised from ethyl alcohol, and obtained in pale yellow prisms melting at 103° :

0.1269 gave 0.3430 CO_2 and 0.0590 H_2O . $\text{C}=73.7$; $\text{H}=5.2$.

$\text{C}_{19}\text{H}_{16}\text{O}_4$ requires $\text{C}=74.0$; $\text{H}=5.2$ per cent.

The solution of the substance in concentrated sulphuric acid is red, and the addition of water produces a pale green precipitate.

Cotarnonideneacetophenone dimethyl ether was obtained by the condensation of cotarnone with resacetophenone dimethyl ether by means of potassium hydroxide in alcoholic solution. It separates in yellow prisms from ethyl alcohol, in which it is sparingly soluble in the cold, and melts at 117° . The bright red solution of this unsaturated ketone in sulphuric acid is formed only momentarily, and quickly becomes orange owing to the production of the sulphate of a pyrrylium base. This was proved by the behaviour of the precipitate and solution obtained on pouring into water, for on the addition of hydrochloric acid a soluble oxonium salt was obtained, and this gave an orange-red platinichloride and picrate.

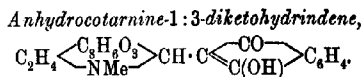


Cotarnine (10 grams) and 1-hydrindone (6 grams) were dissolved in methyl alcohol (20 c.c.), and the solution allowed to remain during a week. On scratching the walls of the containing vessel crystallisation was induced; the substance was then collected and crystallised from benzene and light petroleum, and then again from ethyl acetate, when it was obtained in colourless prisms melting at 126°:

0.1470 gave 0.3887 CO₂ and 0.0809 H₂O. C=72.1; H=6.1.

C₂₁H₂₁O₄N requires C=71.8; H=6.0 per cent.

In properties the compound resembles the analogous anhydrocotarnineacetophenone, being rather more sparingly soluble in the usual solvents. Its salts are stable in aqueous solution, but the base is decomposed by boiling with acetic acid with formation of 1-hydrindone, which was recognised as its semicarbazone melting at 238°.



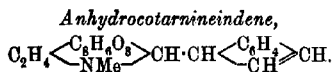
Diketohydrindene (1.9 grams) was ground with a solution of cotarnine (3.8 grams) in methyl alcohol (20 c.c.). The ketone dissolved in the liquid, forming a yellowish-brown solution, from which in a few seconds the new compound separated as a bright, canary-yellow precipitate, which under the microscope was seen to consist of aggregates of small needles. The substance was collected, washed with alcohol, and dried in a vacuum, after which it melted at 188° with vigorous decomposition:

0.1288 gave 0.3279 CO₂ and 0.0652 H₂O. C=69.4; H=5.6.

C₂₁H₁₉O₅N requires C=69.0; H=5.2 per cent.

The compound is sparingly soluble in neutral organic solvents, and recrystallisation is not a profitable process. Its bright yellow colour might suggest that its constitution is analogous to that of benzylidenediketohydrindene, but against this may be cited the fact that the compound is soluble to an orange solution in cold dilute potassium hydroxide and in hot aqueous sodium carbonate. The yellow colour and solubility in alkalis are in agreement with the suggested enolic formula. A solution of the base in dilute acetic acid may be boiled without evident decomposition, and the same is true of its suspension and partial solution in aqueous sodium acetate. When, however, a little sodium acetate is added to a

dilute acetic acid solution, then a crimson colour appears slowly in the cold, but rapidly on boiling. On cooling the colour almost disappears, and a pale yellow, crystalline substance separates from the liquid.



Indene (7 grams) was mixed with cotarnine (14 grams) and methyl alcohol (30 c.c.), and the solution allowed to remain at the ordinary temperature during three days. Water (120 c.c.) and concentrated hydrochloric acid (30 c.c.) were then added, and the liquid boiled and filtered. The cooled solution deposited a quantity of a crystalline hydrochloride, which was recrystallised from hot dilute hydrochloric acid, in which it is remarkably sparingly soluble. The salt crystallises in short, slender needles, and has a beautiful, satiny appearance. It was decomposed with dilute ammonia, and the resulting almost colourless base twice crystallised from methyl alcohol. *Anhydrocotarnineindene* is readily soluble in most organic solvents, but sparingly so in cold methyl alcohol, from which it separates in prismatic needles melting at 136°:

0.1505 gave 0.4125 CO₂ and 0.0860 H₂O. C=74.8; H=6.3.

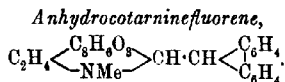
C₂₇H₂₄O₂N requires C=75.2; H=6.3 per cent.

The salts of this base are for the most part sparingly soluble in water; the *sulphate* crystallises from hot dilute sulphuric acid in colourless needles with a satiny appearance.

The Picrate.—This derivative crystallises when alcoholic solutions of its components are mixed. It may be readily recrystallised from ethyl alcohol, in which it is rather sparingly soluble, and forms long, yellow needles, melting and decomposing at 170°:

0.1462 gave 12.4 c.c. N₂ at 13° and 760 mm. N=10.1.

C₂₇H₂₄O₁₀N₄ requires N=9.9 per cent.



Fluorene (7 grams) was left in contact with a solution of cotarnine (10 grams) in methyl alcohol (50 c.c.). After twenty-four hours the liquid was heated until the fluorene had passed into solution, and this process was repeated thrice. Dilute hydrochloric acid was added, and the unchanged hydrocarbon removed by filtration, the acid solution being then basified with ammonia. The viscid precipitate was collected, dissolved in ether, the ethereal solution thoroughly dried, and evaporated nearly to dryness. The

condensation product crystallised slowly from the solution, and was again crystallised from dry ether, and finally from ethyl alcohol. It was so obtained in colourless prisms, melting at 143° with very slight decomposition:

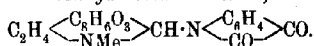
0.1512 gave 0.4303 CO_2 and 0.0815 H_2O . $\text{C}=77.6$; $\text{H}=5.9$.

$\text{C}_{20}\text{H}_{22}\text{O}_3\text{N}$ requires $\text{C}=77.9$; $\text{H}=6.0$ per cent.

The substance is sparingly soluble in neutral solvents, but dissolves readily in dilute hydrochloric acid, and the solution yields the usual sparingly soluble double salts with the appropriate reagents.

The *picrate* is readily obtained on mixing acetone solutions of the base and picric acid. It crystallises in canary-yellow prisms melting at 183° .

Anhydrocotarnineisatin,



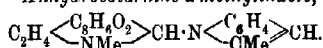
Methyl alcohol (25 c.c.) was poured on a mixture of cotarnine (7 grams) and isatin (4 grams). The solids passed into solution, but very quickly the condensation product separated in orange-red prisms. The substance may be recrystallised from acetone. It is sparingly soluble in alcohol, benzene, or ether, and melts at 146° with vigorous decomposition:

0.1343 gave 0.3213 CO_2 and 0.0617 H_2O . $\text{C}=65.3$; $\text{H}=5.1$.

$\text{C}_{22}\text{H}_{18}\text{O}_5\text{N}_2$ requires $\text{C}=65.6$; $\text{H}=4.9$ per cent.

This compound is a base, but it is decomposed in dilute acid solution, yielding a cotarnine salt and isatin. Cotarnine does not appear to condense with diphenylamine or carbazole.

Anhydrocotarnine- α -methylindole,



A solution of α -methylindole (7 grams) and cotarnine (12 grams) in methyl alcohol (25 c.c.) was allowed to remain overnight, when the whole of the condensation product was found to have separated as a hard, colourless mass, which when broken up resembled porcelain. The substance was dissolved in methyl ethyl ketone and the solution diluted with methyl alcohol, when the compound again crystallised as a hard mass, which was observed under the microscope to consist of prismatic crystals:

0.1350 gave 0.3572 CO_2 and 0.0783 H_2O . $\text{C}=72.1$; $\text{H}=6.4$.

$\text{C}_{21}\text{H}_{22}\text{O}_3\text{N}_2$ requires $\text{C}=72.0$; $\text{H}=6.3$ per cent.

The substance melts at 182° to a red liquid, and is sparingly soluble in most solvents. It dissolves unchanged in dilute hydro-

loric acid to a colourless solution, which has no odour of α -methylindole. On boiling the liquid, decomposition with formation of methylindole and cotarnine slowly occurs, and the same reaction complete and more rapid when the base is boiled with glacial acetic acid. The properties of this and of some other of the substances described above will be subjected to further investigation.

In conclusion, the authors desire to state that much of the expense of this investigation has been met by a grant from the Research Fund of the Chemical Society.

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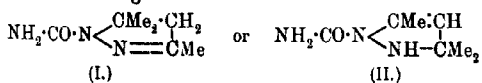
XLV.—Contributions to Our Knowledge of Semicarbazones. Part II. Semicarbazones of Mesityl Oxide.

By FORSYTH JAMES WILSON and ISIDOR MORRIS HEILBRON.

In a previous paper (T., 1912, 101, 1482) the authors have shown that phenyl styryl ketone yields four stereoisomeric semicarbazones, two stable under ordinary conditions and two existing only in alkaline solutions.

In order to investigate the conditions of semicarbazone formation in the case of a simple aliphatic unsaturated ketone, mesityl oxide was selected. A semicarbazone of mesityl oxide was prepared by Scholtz (*Ber.*, 1896, 29, 612), and further investigated by Harries and Kaiser (*Ber.*, 1899, 32, 1338), who obtained it in a purer condition melting at 162–164°.

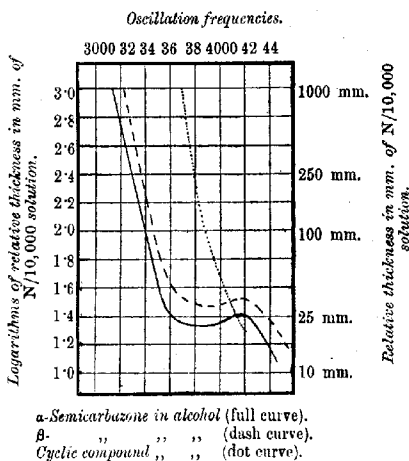
By distillation of this semicarbazone, Scholtz obtained a substance isomeric with it, but incapable of hydrolysis by acid. Harries and Kaiser showed that this isomeric substance melting at 129° was not a stereoisomeric semicarbazone, but a basic compound yielding a picrate, and evidently structurally different from the semicarbazone. These authors, on account of the great stability of this substance, considered that it possessed a cyclic constitution, and proposed the following two formulæ:



These formulæ were discussed later by Rupe and Kessler (*Ber.*,

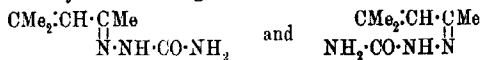
1909, 42, 4503), who proved definitely that formula I was inadmissible, whilst formula II, although probably correct, could not be confirmed.

As, however, two stereoisomeric oximes of mesityl oxide have been obtained, it seemed to the authors that two stereoisomeric semicarbazones should be capable of existence. It was found that these expectations could be realised by exposure of the ordinary semicarbazone (α -form) to ultraviolet light, when it was partly converted into a stereoisomeride (β -form) melting at 133–134°. Conversely, the β -isomeride on exposure to ultraviolet light was partly converted into the α -form. That this new β -isomeride is a



true semicarbazone is shown by the ease with which it is hydrolysed by dilute acid with regeneration of mesityl oxide.

According to theory only two stereoisomerides are possible, as represented by the following formulæ:



The absorption spectra of the α - and β -forms in alcoholic solution are indicated in the figure, the full curve representing the α -form, the dash curve the β -isomeride. Both forms show a shallow band with head at 3900, and are practically identical, as is to be expected from a case of purely nitrogen stereoisomerism.

In the case of the semicarbazones of phenyl styryl ketone (*loc. cit.*), where four stereoisomerides were possible, the effect of light on the solid substances or of alkali on their solutions was to

produce yellow stereoisomerides. In the present case neither semicarbazone was phototropic, nor had alkali any effect on the absorption spectra. Apparently phototropic and thermotropic properties and the shifting to the red of the absorption spectra by alkali require, in the case of semicarbazones, both carbon and nitrogen stereoisomerism. As further proof of this, we have found that with the semicarbazones of cinnamaldehyde and of styryl methyl ketone, where both carbon and nitrogen stereoisomerism are possible, phototropic and thermotropic properties are developed, and also alkali shifts the absorption band towards the red end of the spectrum, whilst semicarbazones of saturated ketones show none of these properties. We hope shortly to publish these results in detail.

The β -modification was distilled in the hope of obtaining a cyclic compound differing from that obtained by Scholtz. The compound obtained, however, was in every way identical with the substance produced by the distillation of the α -form; this can be explained by the fact that we have found that the β -form is unstable, for it was noticed that from specimens of the β -form which had been kept for some time a rise in melting point had occurred. It was found that if the β -form was kept above its melting point for a few minutes it was converted with some decomposition into the α -form. That the cyclic compound melting at 129° is entirely different in constitution from either semicarbazone, is borne out by its absorption spectrum (dotted curve), as shown in the figure.

EXPERIMENTAL.

The mesityl oxide semicarbazone was prepared from mesityl oxide according to the methods of Scholtz (*loc. cit.*) and Rupe and Kessler (*loc. cit.*). The yield of semicarbazone by either method was very variable, even under apparently identical conditions. In some cases, indeed, no semicarbazone at all was produced.

The pure semicarbazone was found to melt sharply at 164°.

β -Modification.—This was obtained from the α -isomeride by exposing it in chloroform solution to a quartz mercury lamp for thirty hours (distance from lamp, 10 cm.). The solution gradually became red and turbid, and was finally separated by filtration from a small amount of an amorphous, red substance. The chloroform was then distilled off, and the residue fractionally crystallised from benzene. The first crop of crystals consisted chiefly of unchanged α -semicarbazone, the more soluble β -modification crystallising out from the mother liquors on concentration. The yield of this isomeride was about 30 per cent., an equilibrium evidently existing between the two forms, for exposure to the ultraviolet light

for longer periods than thirty hours did not increase the yield of this new form.

After a further recrystallisation from benzene the β -semicarbazone was obtained in small, white crystals, melting at $133-134^\circ$, readily soluble in alcohol or hot water, but less so in benzene:

0.1744 gave 40.2 c.c. N_2 at 15° and 758 mm. $N = 27.13$.

0.102, in 14.5 of chloroform, gave $E = 0.153^\circ$. M.W. = 168.

0.201, „ 14.5 „ „ „ $E = 0.320^\circ$. M.W. = 166.

$C_7H_{15}ON_3$ requires $N = 27.09$ per cent. M.W. = 155.

On warming this β -semicarbazone with dilute hydrochloric acid, hydrolysis took place almost immediately with evolution of the readily volatile mesityl oxide vapours.

These results indicate that this β -isomeride is a true semicarbazone, and stereoisomeric with the α -form.

Conversion of the β into the α -Modification.—As it was found previously by us that the semicarbazones of phenyl styryl ketone on exposure to ultraviolet light were interconvertible, it was expected that the same would hold for the α - and β -mesityl oxide semicarbazones. That this assumption was correct was proved by exposing the β -semicarbazone in chloroform solution to ultraviolet light for thirty hours. The solution was then treated as already described, the product on fractional crystallisation from benzene yielding approximately 60 per cent. of the α -isomeride.

The conversion of the β - into the α -stereoisomeride could also be brought about by keeping the β -semicarbazone at a temperature above its melting point ($150-160^\circ$) for some minutes. The fusion was allowed to cool, and, on crystallisation of the dark-coloured solid residue from benzene, a considerable quantity of the α -semicarbazone was obtained.

Preparation of the Isomeric Cyclic Compound melting at 129° .—The substance was prepared by distillation of the α -form as described by Scholtz, and purified by crystallisation from carbon disulphide. On repeating the experiment with the β -semicarbazone, the reaction proceeded in a similar manner, but the yield of the cyclic compound in this case was poor, considerable decomposition taking place, probably during the primary transformation of the β - into the α -isomeride. That the products as obtained from either form were identical was shown by a mixed melting-point determination.

In conclusion, we desire to express our thanks to the Carnegie Trust for the Universities of Scotland for a grant which has defrayed the expenses of this investigation.

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XLVI.—*The Chemical Nature of Some Radioactive Disintegration Products.*

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MANY of the radio-elements have been shown, after close examination, to resemble other elements, and to be non-separable from them by chemical processes; thus the impossibility of separating radio-lead (radium-*D*) from lead, mesothorium-1 and thorium-*X* from radium, ionium and radio-thorium from thorium is well known (Soddy, "Chemistry of the Radio-elements"). The chemistry of the best known disintegration products is summed up by saying that they are identical with such elements as lead in the case of radium-*D*, or as radium in the case of mesothorium-1. Other such resemblances no doubt exist, and in the present paper a systematic investigation has been made of all the radio-elements of period sufficiently long for chemical examination, in the course of which it has been shown that many of the radio-elements known to resemble other elements, either radio-active or inactive, are, in fact, non-separable from them, and several new cases of the same kind have been discovered. The work detailed in this paper increases the number of disintegration products the chemistry of which can be referred to the chemistry of ordinary non-radio-active elements.

Uranium-X.

One of the methods used by Sir W. Crookes (*Proc. Roy. Soc.*, 1900, 66, 409) when he discovered uranium-*X* was to dissolve uranyl nitrate containing a small quantity of an iron salt in excess of dilute ammonium carbonate solution, when most of the iron remained undissolved, and this contained the β -activity due to uranium-*X*. Other methods of separating this substance are known, but until recently these methods have been quite empirical. Among such methods are: (1) Shaking uranyl nitrate, crystallised from water, with ether. The uranyl nitrate dissolves mainly in the ether, whilst the aqueous layer from the water of crystallisation contains the uranium-*X*. (2) Precipitating barium sulphate in a solution of uranyl nitrate. The uranium-*X* is adsorbed by barium sulphate and can be collected with it.

In 1909 Soddy (*Phil. Mag.*, 1909, [vi], 18, 858) collected uranium-*X* from 50 kilos. of uranyl nitrate in a highly concentrated form. The exact nature of the impurities which contained the uranium-*X* was not determined, but it was found possible to dissolve them in concentrated ammonium carbonate, and from the solution so obtained they could be fractionally precipitated by

boiling. In some cases the uranium-X was precipitated almost entirely in the last minute fraction, and in other cases in one of the intermediate fractions. The uranium-X did not seem to follow any general law, but the separation was, as a rule, sharp.

In the same year Ritzel (*Zeitsch. physikal. Chem.*, 1909, 67, 725) found that if charcoal is shaken with a solution of uranium-X the charcoal adsorbs the uranium-X. If, however, a trace of thorium sulphate is present the uranium-X is not adsorbed. Later Marchwald (*Ber.*, 1910, 43, 3421) and Keetman (*Jahrb. Radioaktiv. Elektronik.*, 1909, 6, 265) stated that they had found that they could not separate uranium-X from thorium, but they gave no details of their attempts. If uranium-X and thorium are non-separable, the general explanation of Ritzel's experiment follows at once (Soddy, T., 1911, 99, 72).

The question of the non-separability of uranium-X and thorium by chemical methods was subjected to as rigorous an examination as possible. In doing this one of two methods was used: either a mixture of thorium, another element, and uranium-X was made, and the second element separated as completely as possible from the thorium, after which the β -activities of the two portions were measured, and the relative amounts of uranium-X present in each thus determined; or a mixture of thorium and uranium-X was made, and the thorium separated into fractions by some systematic method, after which the β -radioactivity of the fractions was measured in the electroscope, and then their content of thorium estimated in the usual way gravimetrically, by precipitating an acid solution with oxalic acid, igniting the precipitate, and weighing as thorium oxide. In this way the activity per gram of thorium oxide was obtained. The quantity of uranium-X was always measured by the β -radiation from a thin layer in a standard position with an electroscope which had an aluminium base 0.1 mm. thick.

Uranium-X was separated from uranium with iron, dissolved in dilute acid, and added to a boiling solution of sodium thiosulphate. The sulphur which is thereby precipitated does or does not contain the uranium-X, according as the solution is weakly or strongly acid. Thorium behaves in exactly the same manner. If a mixture of cerium, thorium, and uranium-X was made it was observed that the thorium, whether separated by sodium thiosulphate, hydrogen peroxide, or potassium azoimide, always contained the uranium-X. In a similar manner thorium, separated from zirconium—the mixture containing uranium-X—by dissolving both oxalates in excess of ammonium oxalate and then strongly re-acidifying the solution, contains all the β -activity.

The residues obtained by Soddy (*Phil. Mag., loc. cit.*), from which uranium-X had been separated, ought on this hypothesis to be free from thorium, which was found to be the case. When uranium-X was mixed with them and the mixture fractionated by the ammonium carbonate method, it behaved indefinitely, but when thorium was added its separation with that element was sharp.

It is perhaps worth mentioning that a convenient method for redissolving ignited thorium oxide is to fuse it with sodium peroxide. More than 95 per cent. of thorium oxide was dissolved in one operation, and no appreciable quantity of uranium-X remained undissolved.

Becquerel's original method of separating uranium-X was by adsorption by barium sulphate. If uranium-X and thorium are identical it is to be expected that the adsorption will be inhibited when the latter element is present. Barium sulphate precipitated in a uranium-X solution which contained no thorium carried down 98 per cent. of it, and if this active barium sulphate is boiled with acid no uranium-X passes into solution. A solution of barium, thorium, and uranium-X was treated with sulphuric acid, and the barium sulphate had an activity of one-third of that of the thorium remaining in solution. The filtrate contained thorium and uranium-X, the latter giving a β -activity of 800.9 d.p.m.* per gram of thorium oxide. When the barium sulphate containing one-third of the uranium-X was boiled with nitric acid, the barium sulphate became inactive, and the filtrate contained thorium, which gave an activity due to uranium-X of 778.6 d.p.m. per gram of thorium oxide. The essential difference to be noted is this: if no thorium is present uranium-X cannot be dissolved by boiling with acids when once it has been adsorbed by barium sulphate, but if thorium is present the barium sulphate carried down with it some thorium which can be redissolved by acids, and the concentration of the uranium-X in the two portions of the thorium is constant. The presence of zirconium in a barium and uranium-X solution has no effect whatever on the adsorption by barium sulphate. The presence, however, of cerium inhibits the complete adsorption of uranium-X by barium sulphate, only two-thirds of the uranium-X being adsorbed, but there is this essential difference from the case of thorium, that the uranium-X contained in the precipitated sulphate cannot be redissolved by acids from it.

Boltwood (*Amer. J. Sci.*, 1908, [iv], 25, 269) and others have used the following method of separating uranium and thorium; a mixture of the nitrates is evaporated to dryness at 110°, and then shaken with anhydrous ether. The uranium is stated to pass into

* This refers to divisions per minute in arbitrary units.

solution, whilst the thorium remains undissolved. If this were so, it would be in complete accordance with the observed facts about the completeness of the separation of uranium-X from uranium by the ether method already mentioned. This separation of uranium and thorium has, however, been called into question, and has been the subject of some discussion (Soddy and Pirret, *Phil. Mag.*, 1910, [vi], 20, 345; Mlle. E. Gleditsch, *Le Radium*, 1911, 8, 256). The distribution ratio of uranium and thorium in ether, both anhydrous and containing various quantities of water, has been the subject of a detailed examination, and it has been found that the separation is only complete when small quantities of thorium are present; thus with less than 10 per cent. of thorium nitrate present, no thorium could be detected in the ethereal solution when the mixed nitrates were shaken with one volume of water and ten volumes of ether. Under the conditions of the ether-extraction process for uranium-X there is a relatively large quantity of ether compared with the quantity of water, and a very great weight of uranium compared with the weight of impurities present. Under these conditions no thorium would be dissolved by the ether, and it is known that no uranium-X is dissolved in it. From the solution of a mixture of thorium and uranium nitrates, 50 per cent. of each, it is possible to extract both thorium and uranium-X in the ethereal layer; thus, three successive extractions gave extracts with β -radioactivity corresponding with 10.94, 6.81, and 2.50 d.p.m. respectively, and the concentration of the uranium-X extracted by ether was represented by 129.7 d.p.m. per gram of thorium oxide, whilst that of the uranium-X remaining undissolved was 126.9 d.p.m. per gram of thorium oxide.

A quantity of uranium-X containing iron was dissolved, and about 3 grams of thorium nitrate were added to the solution, which was then treated with excess of ammonium carbonate until the precipitated carbonate was redissolved. This solution was then boiled for a short time, the precipitate collected, and the boiling continued. In this way ten precipitates were formed as follows:

No. of precipitate.	Activity.	Weight of ignited thorium oxalate.	Activity per gram of ignited oxalate.
		Gram.	
1	2.35	0.0380	61.95
2	8.98	0.1711	52.49
3	1.358	0.0225	60.36
4	4.058	0.0643	63.08
5	9.53	0.1499	63.90
6	14.02	0.2214	63.31
7	18.85	0.3026	62.30
8	30.87	0.4967	62.16
9	30.80	0.5221	59.0
10	3.977	0.0701	56.90

It is evident that no alteration in the concentration of uranium-X and thorium has taken place. Another series of fractional precipitations was made, in which the concentration of uranium-X in thorium was more than ten times as great as in the above series, but again it was proved that uranium-X remains uniformly distributed throughout the thorium.

Experiments were now made with fractional crystallisation. Thorium acetate containing uranium-X was dissolved in acetic acid, and the excess of acid slowly evaporated. The first crystals that appeared were removed, and the evaporation continued. In this way three fractions were obtained, which had activities of 169.2, 160.3, and 171.3 d.p.m. per gram of thorium oxide respectively.

Uranium-X is one of the disintegration products that has never been volatilised. One of the methods of dissolving thorium oxide is to volatilise it in a stream of chlorine, when the anhydrous chloride collects in the cooler portions of the furnace. Thorium oxide containing uranium-X was treated in this way, and the product divided itself into three parts: (1) thorium, which collected in the trap outside the furnace, (2) thorium collected in the cooler parts, and (3) thorium which remained unvolatilised. It was found that in none of these portions did the activity per gram of thorium oxide vary more than 4 per cent. from the mean.

Within the errors of experiment in none of these methods has any separation of uranium-X from thorium been effected, although there is no known substance outside the radio-elements which would have remained with thorium through these varied chemical processes.

Radio-actinium.

The usual method employed in the separation of radio-actinium (Hahn, *Ber.*, 1906, **39**, 1605; *Physikal. Zeitsch.*, 1906, **7**, 855) is to precipitate it with sulphur by adding an actinium solution to a boiling solution of sodium thiosulphate, but Hahn has shown that its separation is very uncertain.

Stromholm and Svedberg (*Zeitsch. anorg. Chem.*, 1909, **61**, 338; **63**, 197) have shown that radio-actinium is isomorphous with thorium, and that thorium-X and actinium-X are isomorphous with barium. This does not necessarily mean that thorium and radio-actinium are non-separable elements because radium and barium are isomorphous, yet these two elements can be separated. From analogy to the thorium and the actinium series it is to be expected that radio-actinium will be identical with radio-thorium, and hence with thorium. If this is so, Hahn's thiosulphate method should become sharp and definite in the presence of the smallest quantity of thorium.

The only β -ray substance in the actinium series is actinium-*D*, but the quantity of any of the long-lived substances, actinium, radio-actinium, or actinium-*X*, may be determined by β -ray measurements; thus, if we start with actinium-*X* free from other products the activity due to actinium-*D* rises to a maximum in two hours, and then falls with a period characteristic of actinium-*X*. In the case of a pure preparation of radio-actinium the activity will rise very much more slowly owing to the time required for the production of the intermediate actinium-*X*, and after reaching a maximum should decay to zero. If θ is the time required to reach a maximum value, then:

$$\theta = \log_e \lambda_2 / \lambda_1 / (\lambda_2 - \lambda_1),$$

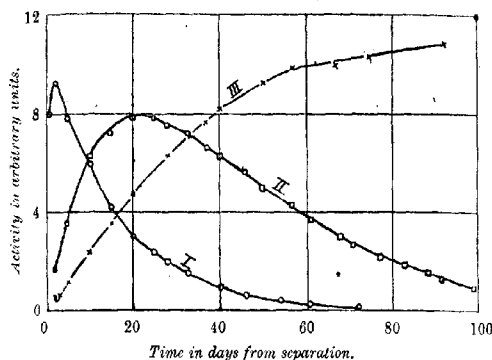
where λ_1 is the radioactive constant of radio-actinium, and λ_2 is the radioactive constant of actinium-*X*. Taking $\lambda_1^{-1} = 28.1$ days, and $\lambda_2^{-1} = 15$ days, θ is calculated to be 20.23 days. From the form of the curves obtained in the various cases the initial purity of the preparation can be deduced quite easily.

About 0.1–0.2 gram of an actinium preparation containing lanthanum was dissolved in acid, and 20 milligrams of thorium nitrate were added. The solution was then rendered alkaline, and the precipitated actinium and thorium hydroxides were collected. The filtrate contained actinium-*X*, which was evaporated to dryness and ignited. The precipitated actinium and thorium hydroxides were redissolved in a slightly acid solution, and added to a boiling solution of sodium thiosulphate. A precipitate of sulphur is formed, and with it the thorium is precipitated as thorium hydroxide. The filtrate from this precipitate was evaporated to dryness and ignited. In this way three preparations were obtained: (1) the evaporated and ignited filtrate from the ammonia precipitation of actinium and thorium hydroxides, (2) the dried and ignited precipitate obtained by sodium thiosulphate, and (3) the evaporated and ignited filtrate from that precipitate. The second preparation will contain the thorium, and its activity should, if it contains radio-actinium, be initially zero, and then rise to a maximum in about twenty days, and finally decay again to zero. The third preparation should contain actinium free from either radio-actinium or actinium-*X*. Its β -activity should also be, initially, zero, but it should rise continually for a number of months. The three preparations were found to behave in the manner indicated (see Fig. 1). The separation of thorium from actinium was also effected with hydrogen peroxide and potassium azoimide, and in each case the β -activity of the precipitated thorium was initially very small, but rose to a maximum in about twenty days, and then

decayed to zero, with a half period of from twenty-five to thirty days.

All the available quantity of actinium was taken, and the radio-actinium separated with a small quantity of thorium by sodium thiosulphate. More thorium was added to this preparation, so that the total quantity of thorium oxide present was about

FIG. 1.



Curve I: Activity of ammonia filtrate—Actinium-X.
 „ II: Activity of thiosulphate precipitate—Radio-actinium.
 „ III: Activity of thiosulphate filtrate—Actinium.

0.2 gram. The whole was dissolved in concentrated ammonium carbonate solution, and then fractionally precipitated by boiling. The activity, measured when it had reached its maximum, per gram of thorium oxide is seen not to vary from a constant value beyond the limits of experimental error.

No. of precipitate.	Activity.	Weight of thorium oxide. Gram.	Activity per gram of thorium oxide.
1	1.512	0.0118	12.81
2	1.614	0.0136	11.86
3	2.258	0.0184	12.25
4	3.398	0.0276	12.30
5	4.565	0.0388	11.92
6	4.748	0.0412	11.53
7	4.496	0.0393	11.84
8	0.596	0.0049	12.17

It has therefore been proved that thorium and radio-actinium are alike in chemical properties so far as they have been examined, and that in place of the separation of radio-actinium from actinium being indefinite, it is effected almost perfectly if a small quantity

of thorium is added to the actinium and the former separated from the latter.

Mesothorium-2.

Hahn (*Physikal. Zeitsch.*, 1908, 9, 246), who discovered this substance, recommends for its separation from mesothorium-1 the use of zirconium. This element is added to a mesothorium solution and precipitated with ammonia, when it carries down the mesothorium-2 with it. In this separation any radiothorium which is present is precipitated with the mesothorium-2.

It is easily shown that mesothorium-2 is not precipitated by hydrogen sulphide, and that therefore it must belong to the third group. It seemed at first that it might be similar to thorium, but it was observed that when thorium is precipitated with potassium azoimide or hydrogen peroxide, mesothorium-2 remains in solution. By dissolving iron, uranium, etc., with mesothorium-2 in ammonium carbonate it was found that it could be concentrated in the more insoluble fractions, and that it was unlike any of the common elements of the third group. The fact that its oxalate was very soluble suggested that it might be similar to actinium. This was tested as follows: If we start with a mixture of mesothorium-2 and actinium free from radio-actinium and subsequent products, the initial activity, if β -rays are measured, will be entirely due to mesothorium-2, which will decay almost completely to zero in two days, in which time exceedingly little actinium-*D* will have grown from actinium. In the course of three or four months actinium-*D* will reach a maximum amount, owing to the radio-actinium and actinium-*X* attaining equilibrium. Therefore, by taking decay curves during the first two days, the relative amount of mesothorium-2 can be found, and, finally, by measuring the activity after equilibrium has been reached the relative amount of actinium present can be ascertained.

Mesothorium-2 was separated from a mesothorium preparation, free from radiothorium, by means of zirconium, and added to a quantity of actinium which had been freed by sodium thiosulphate from radio-actinium (see p. 386). The whole was dissolved in ammonium carbonate and reprecipitated by boiling, and thus divided into several fractions, care being taken that the first fractions were very small. For some time the quantity of actinium-*D* in the fractions was proportional to the quantity of mesothorium-2 that had initially been present, but gradually the quantity of actinium-*D* relative to mesothorium-2 became relatively smaller in the latter fractions, but finally that quantity has again increased until now it is again almost proportional to the quantity of mesothorium originally present.

No. of precipitate.	Activity initially due to mesothorium-2.	Activity due to actinium-D (after 2½ months).	Activity of actinium-D . Activity of mesothorium-2
2	6.13	8.83	1.44
3	25.01	35.31	1.41
4	7.45	9.66	1.28

Precipitates number 1, 5, 6, and 7 were inactive.

Since the quantity of actinium-D is finally proportional to the quantity of actinium present, it is evident that mesothorium-2 has divided itself in the same proportion as actinium. The explanation of the lack of proportionality in the earlier stages of the experiment is that the separation of actinium from thorium is not complete by one precipitation with sodium thiosulphate, and, since it has been shown that radio-actinium is identical with thorium, some radio-actinium remains with the actinium. The solubility of thorium in ammonium carbonate solution is different from that of actinium, so that radio-actinium will not be equally distributed with the actinium, and consequently there will be in the earlier stages of the experiment more actinium-D where radio-actinium has accumulated. It is therefore necessary if a true measure of the quantity of actinium present is required to wait until equilibrium is reached.

Another experiment was made in which actinium free from radio-actinium and actinium-X was dissolved in strongly acid solution along with zirconium containing mesothorium-2. Oxalic acid was added, and the solution gradually neutralised, so that the oxalates were fractionally precipitated. The result at the present time is:

No. of precipitate.	Activity initially due to mesothorium-2.	Activity due to actinium-D (after 2 months).	Activity of actinium-D . Activity of mesothorium-2
2	9.1	3.74	0.41
3	35.0	15.11	0.432
5	61.5	24.96	0.405
6	5.7	1.915	0.375
7	26.75	10.16	0.38
8	12.75	5.43	0.4255

It is to be expected that, as in the preceding experiment, the numbers in the last column will become more nearly equal as complete equilibrium is reached.

Mr. Cranston in this laboratory, who is using the method described for the separation of radiothorium from mesothorium-2, has obtained further evidence in favour of the view here taken that actinium and mesothorium-2 are chemically identical.

Chemistry of the Active Deposits.

Very little is known about the chemistry of the "active deposit group," apart from their relative volatilities in air and other gases (A. S. Russell, *Phil. Mag.*, 1912, [vi], 24, 134), but, on the other hand, considerable progress is being made on the electrochemical side. Evidence of this is seen in von Lerch's rule, that each succeeding substance is electrochemically "nobler" than the last, and in von Hevesy's recent paper (*Phil. Mag.*, 1912, [vi], 23, 628) on their "electrochemistry." Although so little is known there seems to be a fairly general belief that they are allied to the noble metals.

Thorium-*B*, radium-*B*, and actinium-*B* give only a feebly penetrating (β)-radiation, but each gives a *C*-product which gives α -rays. If, therefore, we start with the *B*-member in a pure condition its activity will be initially zero, but will rise to a maximum, and then, since in all cases the *B*-member has a longer period than the *C*-member, the activity will decay to zero with the period of the former. If α -rays are measured, this maximum will be reached in 3.54 hours in the case of thorium-*B*, in 32.78 minutes in the case of radium-*B*, and in 9.29 minutes in the case of actinium-*B*, assuming the usual periods in all cases. If β -rays are measured,* the curves will be substantially of the same form as the α -ray curves, except in the case of actinium, when the maximum for the β -rays will not be reached until a relatively greater time has elapsed, as in this case the *D*-member is longer lived than the *C*-member. If we start with the *C*-member initially pure, then the activity will decay from the beginning with a period of average life of 79, 281, 3.10 minutes, according as the substance is thorium-*C*, radium-*C*, or actinium-*C*.

Thorium-B and Thorium-C.

It was observed that when a solution of a small quantity of lead was added to a solution in which the active deposit group of the thorium series was in radioactive equilibrium; and the lead precipitated completely as sulphide, the precipitate contained thorium-*B* and *C* in equilibrium amount. If the solution was distinctly acid, so that the lead was not completely precipitated, there was excess of thorium-*C* in the quantity of sulphide obtained. If in addition to lead the solution contained tin or other metal the sulphide of which was soluble in ammonium sulphide, then, when that sulphide was removed by this reagent, no activity was found in the solution

* This statement is not strictly true, because radium-*B* gives a small proportion of β -rays (compare Fajans and Makower, *Phil. Mag.*, 1912, [vi], 23, 293).

obtained. This shows that neither thorium-*B* nor -*C* are allied to the noble metals as hitherto supposed. If a solution of lead and copper is precipitated with sodium carbonate and the precipitate digested with potassium cyanide solution, then the copper and any other second group metal present, with the exception of lead and bismuth, will be dissolved as a complex cyanide. In these circumstances, and in the presence of thorium-*B* and -*C*, it was found that no activity was contained in the potassium cyanide solution. This shows that both thorium-*B* and -*C* are similar to lead or bismuth.

A solution of thorium-*B* and -*C* was treated with sulphuric acid and alcohol. The precipitated sulphate was removed, and hydrogen sulphide added to the filtrate to precipitate the bismuth. The activity of the lead sulphate was found to be, at the time of the first measurement, less than one-half of the value that it reached three and a-half hours from the time of precipitation, and by reducing the curves backwards from the time of the first reading until the moment of precipitation it was seen that the value then could not be more than from 8 to 12 per cent. of its maximum value. It is shown, therefore, that lead sulphate contains initially practically no thorium-*C*. On the other hand, the bismuth precipitated as sulphide gave an activity which decayed to half value in twenty-two minutes, and was therefore mainly due to thorium-*C*.

The separation of lead and bismuth containing thorium-*B* and -*C* in solution was effected in the following ways, and the activity of each precipitate measured:

- (1) Lead precipitated as lead sulphate, bismuth as bismuth sulphide.
- (2) Lead precipitated as lead sulphate, bismuth as bismuth hydroxide.
- (3) Lead precipitated as lead chloride.
- (4) Bismuth precipitated as bismuth oxychloride, lead as lead sulphide.
- (5) Bismuth precipitated with *m*-nitrobenzoic acid, lead as lead hydroxide.
- (6) Bismuth precipitated with alcohol.

In each of these cases it was found that the activity of the lead compound rose to a maximum, and then fell to half value in eleven hours, whilst the activity of the bismuth precipitate fell to half value with a period slightly longer than the usual value of thorium-*C*, as a rule about seventy-four to seventy-six minutes. The separation of the two metals was also effected electrolytically by depositing metallic bismuth on the cathode, and lead peroxide on the anode from an acid solution. The activity of the cathode

deposit fell normally with the period of thorium-*C*, but the activity of the anode deposit rose only slightly or not at all before falling with the period of thorium-*B*. On analysis it was found that the lead peroxide contained considerable quantities of bismuth, and that, therefore, it was not possible to deposit lead and bismuth simultaneously in a pure condition.

The reaction mentioned above (No. 5) of separating bismuth by the use of *m*-nitrobenzoic acid is especially interesting. It was suggested by the work of Schlundt and Moore (*J. Physical Chem.*, 1905, 9, 682), who found that thorium-*B* and thorium-*X* remained in solution, whilst thorium and the other products were precipitated by this reagent. Since it appears that thorium-*B* behaves as lead in all the reactions that have been tried, it was of interest to see if the converse is true, if lead will behave as thorium-*B* and will remain in solution, whilst bismuth, if it behaves as thorium-*C*, will be precipitated. This was tested and found to be the case, and a separation of these two metals could be made by this means. The precipitation of bismuth, either by *m*-nitrobenzoic acid or by alcohol, does not seem to be generally known, and it is intended to continue the examination of these two reactions to see if they are capable of application to analytical work.

Experiments were then made in the systematic fractionation of lead in a solution containing thorium-*B* to see if any difference of concentration of thorium-*B* in the various fractions could be noticed. Lead was fractionally precipitated by adding successive small quantities of sulphuric acid and finally alcohol, the precipitate formed being removed between each addition. The activities of the various fractions were measured for two days, and then the quantity of lead sulphate in each fraction was weighed. By dividing the β -activity at any time, after the maximum is reached, measured by the ordinate at that time, by the weight of lead sulphate, the concentration of thorium-*B* in lead sulphate at that time is obtained.

No. of precipitate.	Weight of lead sulphate. Gram.	Activity at 5 p.m.	Activity per gram of lead sulphate at 5 p.m.	Activity at 11 a.m. next day.	Activity per gram at 11 a.m. next day.
1	0.1161	0.90	7.26	0.29	2.486
2	0.2879	2.086	7.26	0.68	2.360
3	0.1810	1.28	7.09	0.374	2.064
4	0.0894	0.65	7.29	0.225	2.51
5	0.0501	0.456	9.1	0.15	2.99

The last two columns are merely confirmatory evidence of the constant distribution of thorium-*B* throughout the lead. Lead was fractionally crystallised as chloride, and also fractionally volatilised

as chloride, and in each case similar series to the one shown above were obtained, showing that it was not possible to alter the concentration of thorium-*B* in lead.

Thorium-*C* was fractionally precipitated with bismuth in two ways. The bismuth was dissolved in concentrated ammonium carbonate, and then reprecipitated by boiling. In every experiment that was made a very small concentration from the bismuth was observed in the opposite sense to that which would have occurred with polonium. The second method was by fractional precipitation of the oxychloride, and again a very small concentration was observed, thorium-*C* being more soluble than bismuth. The concentration of the first portion was 1.735 units of activity per gram of bismuth oxide, whilst that of the second portion was 1.88. The difference in concentration is very small, and is probably capable of the simple explanation that there is present a small quantity of thorium-*B* which produces thorium-*C* in the interval between the precipitations.

Radium-B and Radium-C.

In the same way as has been shown with thorium-*B* and -*C*, radium-*B* and -*C* were found to be similar to lead and bismuth respectively, to the exclusion of all other elements. A solution of the active deposit of rapid change, containing in addition lead and bismuth, was treated in the following ways so that these two metals were separated:

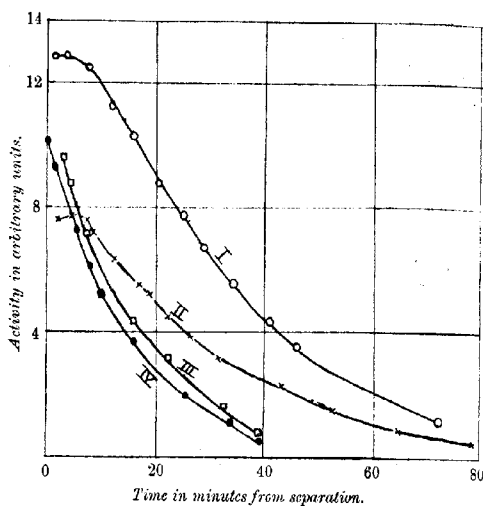
- (1) Lead precipitated as lead sulphate, bismuth precipitated as bismuth sulphide.
- (2) Lead precipitated as chloride.
- (3) Bismuth precipitated as bismuth oxychloride, lead as lead hydroxide.
- (4) Bismuth precipitated with *m*-nitrobenzoic acid.
- (5) Bismuth precipitated as metal on the cathode, lead precipitated as lead peroxide on the anode.

The curves obtained (see Fig. 2) show that the activity of the lead precipitates decay to half value in thirty-six minutes, whilst the bismuth precipitates decay to half value in from twenty to twenty-two minutes, showing that the activities, in the first case, were due to radium-*B*, and in the second case, to radium-*C*. If the preparation of radium-*B* is pure initially, the activity ought to rise to a maximum in 32.87 minutes after separation. The form of the curves showed that the activities of the substances contained the lead was falling from a maximum value, but even by precipitating lead sulphate, collecting it, and drying it within ten minutes was not possible to get a very definite rise to a maximum.

Owing to the shortness of the periods of both substances it was found impossible to make determinations of their behaviour on fractional treatment.

The results of these experiments are therefore that in all the reactions which it was possible to try it was observed that radium-*B* behaves as lead, and that radium-*C* behaves as bismuth. Consider-

FIG. 2



Curve I: Activity obtained in lead sulphate—Radium-B.
 „ II: Activity of lead peroxide on anode—Radium-B.
 „ III: Activity of bismuth on cathode—Radium-C.
 „ IV: Activity of ppt. with m-nitrobenzoic acid—Radium-C.

ing the known similarity between the corresponding members of the active deposit groups, it is most probable that radium-*B* and radium-*C* are chemically non-separable from lead and bismuth in the same way as thorium-*B* and thorium-*C* have been shown to be.

Actinium-B and Actinium-C.

In the case of these two substances the same experiments were made as with radium-*B* and radium-*C*, and it was observed that similarly they were like lead and bismuth respectively.

The activity of the lead precipitated from a solution of actinium active deposit either as lead sulphate, lead chloride, lead sulphide, or lead peroxide on the anode decayed to half value in thirty-eight

minutes. In this case the activity of a lead precipitate, if it, initially, contains pure actinium-*B*, should reach a maximum value in 9.29 minutes. It was not possible to observe this maximum, and all the precipitates obtained were, by the time they could be dried and measured, decaying exponentially.

The decay of actinium-*C* could be measured in bismuth obtained as a precipitate with *m*-nitrobenzoic acid or by deposition of metallic bismuth on the cathode. Bismuth which was obtained in this way had an activity which decayed to half value in something less than three minutes. These measurements were made with α -rays. Enough actinium was not available to obtain a sufficient quantity of the products for β -ray measurements, so that it is, at the moment, not possible to say anything about the chemical behaviour of actinium-*D*.

The conclusions that were drawn with respect to radium-*B* and -*C* are equally applicable here, namely, that in all the reactions that have been tried no evidence of the separation of actinium-*B* and actinium-*C* from lead and bismuth has been obtained, and it is probable that they are chemically similar to these elements.

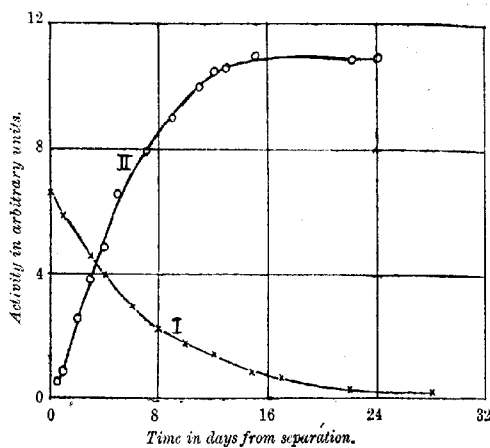
Radium-E.

Radium-*E* was for a long time considered to be a complex substance owing to the work of Rutherford (*Phil. Mag.*, 1904, [vi], 8, 636) and of Meyer and von Schweidler (*Sitzungsber. K. Akad. Wiss. Wien*, 1906, iia, 115, 697), but later work due to Antonoff (*Phil. Mag.*, 1910, [vi], 19, 825) has shown it to be a single substance. This work shows that a substance with a period of average life of 7.25 days followed radio-lead, but no evidence has yet been given to show whether polonium is the direct product of radium-*E*.

A sample of radio-lead containing large quantities of lead was precipitated with sulphuric acid. By one precipitation radio-lead is freed from about 80 per cent. of its β -ray activity. By dissolving this sulphate in ammonium acetate, reprecipitating with hydrogen sulphide, redissolving in acid, and finally reprecipitating with sulphuric acid, radio-lead is obtained practically free from β - or α -ray activity. Measurements were then made with the apparatus used by Soddy (*Phil. Mag.*, 1909, [vi], 18, 858) to attempt to detect a growth of α -radiation from uranium-*X*, in which the powerful β -radiation was suppressed by placing the preparation between the poles of a magnet. The electroscope was of brass, and had in its base an opening 9 cm. long by 1.75 cm. broad, which was covered with aluminium foil 0.0031 mm. thick. Across this opening, arrangements were made for pushing over or withdrawing a piece

of mica 0.05 mm. thick. The preparations were on a thin layer of filter paper, contained in a tray 8×1.5 cm., which was placed between the poles of the electromagnet, and was 0.5 cm. below the aluminium foil. If the magnet was off and the mica foil across the opening, all the α -rays would be absorbed, and only β -rays and a small quantity of γ -rays would reach the ionising chamber. If the magnet was on and the mica away from the opening, most of the ionising effect would be due to α -rays, but there would be a small effect due to undeviated β -rays and the small quantity of

FIG. 3.



Curve I: Decay of β -rays of radium-E.

„ II: Growth of α -rays of radium-F.

(Note.—Curve II is on a larger scale than Curve I.)

γ -rays. The growth of α - and β -rays from two preparations of radio-lead was measured with (1) radio-lead precipitated twice as lead sulphate, and (2) radio-lead crystallised twice as lead chloride. The curves agree with those calculated from the view that the only intermediate member between radium-D and radium-F is radium-E with a period of 7.25 days.

The simultaneous decay of radium-E and growth of polonium was also observed. The purest radium-E was obtained by separating by two crystallisations of lead chloride both radium-E and polonium from a relatively large quantity of radio-lead. The separation was then repeated after two days had elapsed, and the last fractions of lead were removed as sulphate. A rod of bismuth was then immersed in the filtrate for three or four hours. In this

way a strong β -ray preparation with an α -activity less than one-tenth of the β -ray activity was obtained. The β -ray activity decayed to half value in five days, whilst the α -ray activity increased according to the $I_t/I_\infty = 1 - e^{-\lambda t}$ law, showing that the α -ray substance was produced directly from radium-*E*. There is thus no evidence of any intermediate substances except radium-*E* between radio-lead and polonium (see Fig. 3).

The chemical nature of radium-*E* was then studied, and it was found to be in all respects similar to bismuth. It was found to remain with the bismuth when that substance was precipitated, after the removal of the lead from a radio-lead solution, by hydrogen sulphide, ammonia, or dilute ammonium carbonate, and with the bismuth when that element was precipitated from a radio-lead solution by *m*-nitrobenzoic acid or as bismuth oxychloride. Fractional precipitation experiments were also made by precipitating, by boiling, bismuth carbonate dissolved in concentrated ammonium carbonate. The decay curves were taken, and then the bismuth estimated gravimetrically as oxide.

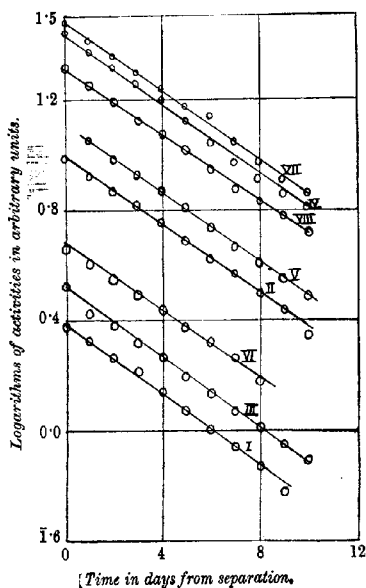
No. of precipitate.	Weight of bismuth oxide. Gram.	Activity of precipitate on October 23rd.	Activity per gram on that date.	Activity of precipitate on October 29th.	Activity per gram on that date.
1	0.1399	3.732	2.67	1.536	1.099
2	0.0920	2.377	2.53	1.033	1.120
3	0.0496	1.323	2.72	0.6054	1.215
4	0.0125	0.3356	2.68	0.1356	1.084

The last two columns confirm the regular decay of radium-*E*.

The conclusions of Rutherford already referred to concerning the complex nature of radium-*E* were arrived at by a consideration of the activities shown by the volatilised and unvolatilised parts of radium-*E* collected from radium emanation on a platinum wire. Experiments were therefore made in the volatilisation of bismuth compounds, for example, bismuth sulphide, bismuth chloride, and bismuth iodide. A strong preparation of radium-*E* had a little bismuth added to it, the whole being dissolved, precipitated as carbonate, and ignited in the filter paper, so that the oxide was reduced to metal. This was thoroughly ground with a quantity of iodine, placed at the bottom of a long, hard glass test-tube, and heated. Bismuth iodide was formed, which volatilised and condensed over a considerable length of tube. The tube was then divided into a number of sections. One section had a particularly strong activity, and the volatilisation process was repeated for it alone. In this way eight fractions were obtained, the radiation of which without exception decayed to half value in from 5.0 to 5.2 days. The logarithmic curves are given in Fig. 4. As the total

quantity of bismuth was equivalent to only about 0.05 gram of bismuth oxide, the amount of bismuth in each fraction was very small, and thus it was not possible to get an exact determination of the concentration of radium-E, but there was no distinct alteration in the proportion of radium-E to bismuth in any of the fractions. Had there been any other substance present, such as a

FIG. 4.



Lines are logarithmic decay curves of radium-E, and are numbered in the order of the volatilities.

second intermediate substance between radio-lead and polonium, it would have shown itself in a difference between the decay curves of the first and last fractions. No such difference was observed.

Summary.

It has been shown that uranium-X and radio-actinium are chemically similar to, and non-separable from, thorium; mesothorium-2 is non-separable from actinium; thorium-B is non-separable from lead; radium-B and actinium-B are extremely similar to lead, and most probably non-separable from it; thorium-C, radium-C, and

actinium-*C* are very closely allied to bismuth, and probably chemically similar to it. The present view that there is only one product, namely, radium-*E*, between radio-lead and polonium, has been confirmed by the direct measurement of the growth of radium-*F* from radium-*E*; finally, radium-*E* has been shown to possess chemical properties identical with those of bismuth in all respects.

I desire to thank Mr. F. Soddy, F.R.S., for suggesting this research, for his interest in it throughout its entire course, and for the use of materials employed in carrying it out.

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XLVII.—*The Identification of Ipuranol and Some Allied Compounds as Phytosterol Glucosides.*

By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

THE compound designated as ipuranol was first isolated in these laboratories in 1908 from the stems of *Ipomoea purpurea*, Roth (Nat. Ord. *Convolvulaceae*), received from South Africa (*Amer. J. Pharm.*, 1908, **80**, 264). The amount of substance obtained from this source was so small as to permit only of determining its empirical composition, melting point ($285-290^{\circ}$), and the melting point of its acetyl derivative (160°). At about the same time, however, an evidently identical substance was isolated from olive bark (T., 1908, **93**, 907), and as in this instance both the substance (m. p. $285-290^{\circ}$) and its well-crystallised acetyl derivative (m. p. 160°) were analysed, it was concluded that ipuranol is a dihydric alcohol, possessing the formula $C_{28}H_{48}O_2(OH)_2$. The analytical figures obtained for both these compounds were, in fact, in excellent agreement with this assumption. In the same year a very small amount of a similar substance was obtained from nutmeg (*Amer. J. Pharm.*, 1908, **80**, 575), which, however, could only be obtained sufficiently pure for analysis in the form of its acetyl derivative (m. p. $163-164^{\circ}$). It was first in this connexion that the substance was observed to yield a colour reaction similar to that given by the phytosterols.

In the intervening years a considerable further number of substances have been isolated from widely different sources, which either agreed in composition with the formula assigned to

ipuranol, or which differed from the latter in their characters and composition only to such an extent as to cause them to be regarded as homologous compounds. To these apparently related substances the following distinctive names and formulæ were assigned: citrullol, $C_{22}H_{36}O_2(OH)_2$, melting at $285-290^\circ$ (T., 1910, **97**, 102), and trifolialol, $C_{21}H_{34}O_2(OH)_2$, melting at 295° (T., 1910, **97**, 249). These two substances, together with ipuranol, were thus considered to be members of a series of dihydric alcohols, represented by the general formula $C_nH_{2n-6}O_4$.

Another group of substances had meanwhile been obtained, which were likewise regarded as dihydric alcohols, and yielded colour reactions similar to those given by the phytosterols. These compounds, however, differed appreciably from the members of the ipuranol series by their greater facility of crystallisation and a generally lower melting point, as also to some extent in their percentage composition. The first member of this class of compounds was isolated from jalap tubers (*Ipomoea purga*, Hayne), and to it the name ipurganol (m. p. $222-225^\circ$) and the formula $C_{21}H_{32}O_2(OH)_2$ were respectively assigned (*J. Amer. Chem. Soc.*, 1910, **32**, 89). Various closely related substances which, together with ipurganol, appeared to constitute a series of dihydric alcohols represented by the general formula $C_nH_{2n-8}O_4$, were given the following distinctive names and formulæ: bryonol, $C_{22}H_{34}O_2(OH)_2$, melting at $210-212^\circ$ (T., 1911, **99**, 943); grindelol and anonol, $C_{23}H_{36}O_2(OH)_2$, melting at $256-257^\circ$ and $294-298^\circ$ respectively (*Proc. Amer. Pharm. Assoc.*, 1907, **55**, 342, and *Pharm. J.*, 1911, **87**, 744); and cucurbitol, $C_{24}H_{38}O_2(OH)_2$, melting at 260° (*J. Amer. Chem. Soc.*, 1910, **32**, 36). A substance, melting at 245° , to which the name of calabarol has been given (T., 1911, **99**, 2155), was considered to possess the formula $C_{23}H_{34}O_2(OH)_2$, and therefore to be the first representative of dihydric alcohols having the general formula $C_nH_{2n-10}O_4$.

Quite recently Tutin and Clewer (T., 1912, **101**, 2230) isolated from *Cluytia similis*, Muell. Arg. (Nat. Ord. *Euphorbiaceae*), a substance which was observed to resemble ipuranol and other related compounds in its general characters, and was designated cluytialol. It was subsequently obtained in larger amount from taraxacum root (T., 1912, **101**, 2426). This substance (m. p. $300-305^\circ$) was first regarded as a trihydric alcohol, $C_{23}H_{37}O(OH)_3$ (P., 1912, **28**, 265), but a comparison of the figures obtained by its analysis and the analysis of its acetyl and benzoyl derivatives, together with a molecular-weight determination of the acetyl derivative, subsequently led the above-mentioned authors to regard cluytialol as a tetrahydric alcohol, having the formula $C_{23}H_{40}O(OH)_4$ (P., 1912,

28, 317). At the same time, and with similar considerations, ipuranol was thought to be more correctly represented as a trihydric alcohol, having the formula $C_{20}H_{47}O_2(OH)_3$, instead of $C_{25}H_{38}O_5(OH)_2$, as originally adopted.

The amounts of the various above-mentioned compounds which have hitherto been isolated were in most cases comparatively small, and, with a few exceptions, did not permit of the analysis of their derivatives. The characters of the substances nevertheless rendered it evident that they represented a new class of compounds, and as they gave well-crystallised acetyl and benzoyl derivatives, having definite melting points, it was apparent that they were of alcoholic nature. It may also be noted that, although ipuranol was first obtained from an ethyl acetate extract of the resinous constituents of the respective plant, it has subsequently, as well as the related compounds, been isolated either from the petroleum or the ether extract of the resin. In one instance (citrullol, *loc. cit.*), the substance was separated from an aqueous liquid, in which it appeared to be contained in a colloidal state. Furthermore, in a considerable number of cases the various compounds were isolated from a petroleum extract of the resinous constituents after the extract had been heated for some time with an alcoholic solution of potassium hydroxide, and this fact seemed especially to confirm the view respecting the alcoholic nature of the compounds.

It has naturally been deemed desirable to obtain, if possible, some further information regarding the character of the numerous compounds here considered, but the small amounts of material hitherto available had precluded any extended experiments in this direction. Some recent observations, however, have served to reveal the nature of the compounds in question, inasmuch as it has been found that several of them, when heated in amyl-alcoholic solution with aqueous hydrogen chloride, become hydrolysed with the formation of a phytosterol and dextrose. It is thus evident that the substances are phytosterol glucosides, and their percentage composition is also in harmony with this view.

In order that the results obtained by the analysis of these various compounds and some of their derivatives, as previously recorded, may be compared with the calculated percentage figures of phytosterol glucosides and the respective acetyl and benzoyl derivatives of the latter, they have been arranged in a tabular form, and at the same time the source of the compounds has been indicated, together with the names and formulæ hitherto assigned to them.

In addition to the list on p. 402, substances resembling ipuranol have also been obtained from the fruit of *Ecballium Elaterium*

(T., 1909, 95, 1988) and from the bark of *Erythrophloeum Guineense* (Amer. J. Pharm., 1912, 84, 348), but not in amounts sufficient for analysis.

Name and formula.	Source.	M.p. and analysis.		M. p. and analysis of acetyl derivative.	
		C.	H.	C.	H.
Ipuranol, $C_{27}H_{46}O_4$	<i>Ipomoea purpurea</i>	285—290°.	72·6; 10·6	160°.	—
"	Olive bark	285—290°.	72·6; 10·6	160°.	66·5; 9·4
"	Nutmeg	—	—	163—164°.	69·5; 9·4
"	<i>Prunus serotina</i> , bark	285—290°.	72·3; 10·7	160°.	—
"	" " leaves	295°.	—	163°.	—
"	<i>Apocynum androsaemifolium</i>	285—290°.	72·4; 10·5	162°.	—
"	<i>Rumex Ecklonianus</i>	285—290°.	—	162°.	—
"	<i>Ornithogalum thyrsoides</i>	285—290°.	72·3; 10·5	162°.	—
"	<i>Gelsemium sempervirens</i>	290°.	72·3; 10·5	162°.	—
"	<i>Iris versicolor</i>	285—290°.	72·3; 10·3	162—163°.	—
"	<i>Withania somnifera</i>	285—290°.	72·4; 10·3	164—165°.	—
"	<i>Euphonia ditricha</i>	285°.	—	—	—
"	<i>Oenanthe crocata</i>	285—290°.	—	161°.	—
"	<i>Casimiroa edulis</i>	290—295°.	72·6; 10·4	166°.	69·7; 9·3
"	<i>Ipomoea orizabensis</i>	285—290°.	72·4; 10·6	162°.	—
"	Scammony root	285—290°.	72·2; 10·6	162°.	—
Citrullol, $C_{27}H_{38}O_4$	<i>Colocynth</i>	285—290°.	72·0; 10·6	167°.	69·3; 9·2
"	<i>Euvonyma atropurpurea</i>	285—290°.	71·0; 10·7	164—165°.	69·0; 9·2
"	<i>Caulophyllum thalictroides</i>	275—280°.	71·9; 10·4	169—170°.	—
Trifolanol, $C_{21}H_{36}O_4$	<i>Trifolium pratense</i>	285°.	71·4; 10·4	166—166°.	68·8; 9·2
"	" incarnatum	295—300°.	71·5; 10·4	165—166°.	68·6; 9·2
Calabarol, $C_{27}H_{36}O_4$	Calabar bean	945°.	73·1; 10·1	—	—
Ipurganol, $C_{27}H_{34}O_4$	<i>Ipomoea purga</i>	222—225°.	71·7; 10·0	166—167°.	68·9; 8·8
Bryonol, $C_{23}H_{36}O_4$	Bryony root	210—212°.	72·3; 10·1	163°.	69·1; 9·0
Grindelol, $C_{23}H_{38}O_4$	<i>Grindelia camporum</i>	257°.	72·7; 10·2	161°.	—
Anonol, $C_{23}H_{38}O_4$	<i>Anona muricata</i>	294—295°.	72·9; 10·3	166°.	—
Cucurbitol, $C_{24}H_{40}O_4$	Watermelon seed	200°.	73·2; 10·4	150°.	—
Cluytianol, $C_{26}H_{40}O_5$	<i>Cluytia similis</i>	300—305°.	72·3; 10·5	160°.	68·7; 9·1
"	Taraxacum root	297°.	72·5; 10·6	161°.	68·6; 9·1

In a few instances benzoyl derivatives of the above-mentioned compounds were prepared, which had the following characters: Benzoylipuranol, from *Oenanthe crocata* and *Casimiroa edulis*, melting at 196° and 197° respectively; benzoylanonol, m. p. 197—198°. C=75·9; H=7·8; benzoylcalabarol, m. p. 195—196°. C=76·1; H=7·8; benzoylcluytianol (from *Cluytia similis*), m. p. 192°. C=76·3; H=7·7; (from taraxacum root), m. p. 196°. C=76·2; H=7·9 per cent.

It is well known that a considerable number of isomeric phytosterols occur in nature which possess the formula $C_{27}H_{46}O$, whilst other compounds of this type are represented by the formula $C_{30}H_{50}O$ (or $C_{30}H_{48}O$) and $C_{20}H_{34}O$. As examples of these different classes there may be noted: sitosterol, $C_{27}H_{46}O$ (Monatsh., 1897, 18, 551), stigmasterol, $C_{30}H_{50}O$ or $C_{30}H_{48}O$ (Ber., 1906, 39, 4378), and rhamnol, $C_{20}H_{34}O$ (Proc. Amer. Pharm. Assoc., 1904, 52, 299). The glucosides and their acetyl and benzoyl derivatives of the first two types of phytosterols mentioned would have the following composition respectively:

Sitosterol Glucoside and Derivatives.

$C_{53}H_{86}O_6$ requires C=72·3; H=10·2 per cent.

$C_{53}H_{82}O_6(CO \cdot CH_3)_4$ requires C=68·7; H=8·9 per cent.

$C_{53}H_{82}O_6(CO \cdot C_6H_5)_4$ " C=75·9; H=7·5 " "

Stigmasterol Glucoside and Derivatives.

$C_{36}H_{50}O_6$ requires C=73.5; H=10.2 per cent.

$C_{36}H_{50}O_6(CO \cdot CH_3)_4$ requires C=69.8; H=9.0 per cent.

$C_{36}H_{50}O_6(CO \cdot C_6H_5)_4$ " C=76.5; H=7.6 " "

A comparison of these figures with those afforded by the analysis of the above-mentioned, naturally occurring compounds renders it probable that a considerable proportion of the latter are glucosides of sitosterol or one of its isomerides, whilst in some cases their composition would appear to approximate more closely to that of a stigmasterol glucoside. Inasmuch as different phytosterols are frequently found in the same plant, it is to be expected that their respective glucosides may also occur in the form of mixtures, and these would be exceedingly difficult to separate. The possibility of different sugars being united with the phytosterol complex is also not excluded.

In this connexion it may incidentally be noted that H. and A. Euler (*Ber.*, 1907, 40, 4762) obtained from the varnish-like coating of the leaves of the common alder (*Alnus glutinosa*, Gaertn.) a substance which they designated glutinolic acid, and which was stated to give an intense cholesterol (phytosterol) reaction. To this substance, which was obtained only in an amorphous state, they assigned the formula $(C_{28}H_{48}O_6)_x$, which requires C=72.4; H=10.3 per cent. These figures are in such close agreement with those required for a sitosterol glucoside that, together with the colour reaction noted, it appears probable that the so-called "glutinolic acid" consisted essentially of a compound of the above-described type. The method by which the substance was obtained, together with its low melting point, likewise suggests that the observed acidic properties may have been due to its contamination with a small amount of a fatty acid.

EXPERIMENTAL.

It had previously been observed that some of the compounds under consideration were not altered by heating with aqueous hydrogen chloride in the presence of a little alcohol, but this result was evidently due to their sparing solubility, and did not preclude the possibility of their being glucosidic. As the compounds, however, were soluble in warm amyl alcohol, it was found that their hydrolysis could be effected by the use of this solvent. Such of them as were at present available in sufficient amounts have therefore now been examined in the direction indicated, and with the following results:

I. *Ipuranol* (m. p. 290—295°). A typical specimen of this substance had the following composition:

0.1147 gave 0.3039 CO_2 and 0.1084 H_2O . $\text{C}=72.3$; $\text{H}=10.5$.

The formula originally assigned to ipuranol, namely, $\text{C}_{23}\text{H}_{40}\text{O}$, requires $\text{C}=72.6$; $\text{H}=10.5$ per cent.

Sitosterol glucoside, $\text{C}_{33}\text{H}_{56}\text{O}_6$, requires $\text{C}=72.3$; $\text{H}=10.2$ per cent.

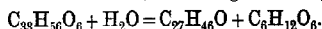
Half a gram of the substance was dissolved in 30 c.c. of hot amyl alcohol, and 10 c.c. of an aqueous 15 per cent. solution of hydrogen chloride added, together with sufficient ethyl alcohol to form a homogeneous liquid. After heating for two hours in a reflux apparatus, steam was passed through the mixture to remove the amyl alcohol, and the contents of the flask then filtered. A solid substance was thus collected, which, when crystallised from a mixture of alcohol and ethyl acetate, separated in glistening leaflets melting at 136°. This substance gave the phytosterol colour reaction, and it evidently belonged to that class of compounds:

0.1041 gave 0.3204 CO_2 and 0.1127 H_2O . $\text{C}=83.9$; $\text{H}=12.0$.

$\text{C}_{27}\text{H}_{46}\text{O}$ requires $\text{C}=83.9$; $\text{H}=11.9$ per cent.

The aqueous acid liquid, from which the phytosterol had been separated by filtration, was exactly neutralised with sodium carbonate, evaporated to dryness, the residue digested with absolute alcohol, and the mixture filtered. On evaporating the alcoholic filtrate a small amount of a syrupy residue was obtained, which reduced Fehling's solution, and yielded an osazone melting and decomposing at 212°. It was thus evident that the sugar consisted of dextrose.

The original compound had thus become resolved by hydrolysis into a phytosterol and dextrose, according to the equation:



II. *Ipuranol* (m. p. 280—285°). This specimen of the substance was obtained from a different source from the preceding one, and it gave on analysis the following result:

0.0973 gave 0.2573 CO_2 and 0.0918 H_2O . $\text{C}=72.1$; $\text{H}=10.5$.

$\text{C}_{33}\text{H}_{56}\text{O}_6$ requires $\text{C}=72.3$; $\text{H}=10.2$ per cent.

Half a gram of this substance was hydrolysed in the manner above described, when it yielded a phytosterol, which separated in glistening leaflets, melting at 136°. This was analysed, and its specific rotatory power determined:

0.0911 gave 0.2800 CO_2 and 0.1002 H_2O . $\text{C}=83.8$; $\text{H}=12.2$.

$\text{C}_{27}\text{H}_{46}\text{O}$ requires $\text{C}=83.9$; $\text{H}=11.9$ per cent.

0.2649 of anhydrous substance, made up to 20 c.c. with chloroform, gave $\alpha_D - 0^\circ 56'$ in a 2-dcm. tube, whence $[\alpha]_D - 35.2^\circ$.

The aqueous acid liquid obtained by the hydrolysis was found to contain a sugar, from which *d*-phenylglucosazone (m. p. 212°) was prepared.

III. *Citrullol* (m. p. 285—290°). This represented the compound which had previously been isolated from colocynth (T., 1910, 97, 102). A small amount (0.15 gram) of its acetyl derivative was hydrolysed in the above-described manner, when it yielded a phytosterol which separated from a mixture of alcohol and ethyl acetate in small needles, melting at 145—149°. The sugar produced by the hydrolysis gave an osazone which, in the crude state, melted at 190—192°, but the amount was too small to permit of its purification.

IV. *Bryonol* (m. p. 210—212°). The compound to which this name had been assigned was obtained from bryony root (T., 1911, 99, 943). A small amount (0.15 gram) of the substance, when hydrolysed in the manner above described, yielded a phytosterol which separated from a mixture of alcohol and ethyl acetate in leaflets, melting at about 90—100°. When recrystallised from alcohol it was obtained in small tufts of needles, which sintered at 90° and melted completely at 105°. The same melting point was observed after it had been kept in a vacuum desiccator for forty-eight hours. The phytosterol dissolved completely in concentrated sulphuric acid with a yellow colour and green fluorescence, and evidently differed from sitosterol. A small amount of sugar was likewise produced by the hydrolysis, and this was found to reduce Fehling's solution, but it was not sufficient for the preparation of an osazone.

V. *Cluytianol* (m. p. 297°). The specimen of this compound which served for its present examination was obtained from taraxacum root (T., 1912, 101, 2426). A small amount (0.2 gram) of the substance was hydrolysed as above described, when it yielded a phytosterol which crystallised in glistening leaflets, melting at 136°. The sugar produced by the hydrolysis was found to reduce Fehling's solution, but was not sufficient in amount for the preparation of an osazone.

Although it has not been possible to subject all the compounds enumerated in the preceding list to the above-described treatment, the results which are now recorded are deemed quite sufficient to lead to the conclusion that they are all phytosterol glucosides. Such compounds had not previously been known to occur in nature, and it may be regarded as of some significance that in practically all instances where their isolation had been effected phytosterols of varying character had also been found. With consideration of the

facts which have thus been elicited respecting the nature of the compounds in question, it is not deemed desirable that distinctive names should be perpetuated for them, but that they should receive some collective designation, and it is therefore proposed that they be termed *phytosterolins*. The future examination of compounds of this type, when available in sufficient amounts, would appear to be most suitably directed to the characterisation of the phytosterols which they yield on hydrolysis, and also, when possible, to that of the sugar produced.

It may finally be noted that some recent experiments, conducted by one of us, have led to the synthesis of sitosterol-*d*-glucoside, which has been found to possess properties agreeing with those of the substance designated as ipuranol. The details of these experiments will form the subject of a further communication.

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LONDON, E.C.

XLVIII.—*The Absorption Spectra of Substances Containing Labile Hydrogen Atoms.*

By PETER JOSEPH BRANNIGAN, ALEXANDER KILLEN MACBETH,
and ALFRED WALTER STEWART.

THE absorption spectra of ethyl acetoacetate and some of its derivatives were examined by Magini (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 104), and by Baly and Desch (T., 1904, 85, 1029; compare T., 1905, 87, 766). The last-named authors put forward certain views to account for their results. This work has been repeated and much extended by Hantzsch (*Ber.*, 1910, 43, 3049), who has thrown very grave doubt on the assumptions made by Baly and Desch. In the present paper the spectra of various compounds which contain hydrogen atoms replaceable by sodium have been examined with the view of increasing our knowledge of simple substances containing such groupings. The results obtained tend to confirm the correctness of Hantzsch's views.

Baly and Desch observed that in alcoholic solution ethyl acetoacetate shows only general absorption; the enolic derivative, ethyl ethoxycrotonate, $\text{CH}_3\cdot\text{C}(\text{OEt})\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, shows no selective absorption; nor does what they call "the keto-substance ethyl ethyl-acetoacetate," $\text{CH}_3\cdot\text{CO}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$. When, however, alkali is added to an alcoholic solution of ethyl acetoacetate an absorption

band appears in the spectrum, and attains greater and greater persistence as the relative amount of alkali present is increased, until at last a maximum persistence of band is obtained, beyond which no further change in the spectrum occurs, even when more alkali is added to the solution. Similar bands were found in the spectra of metallic derivatives of acetylacetone and the aluminium derivative of ethyl acetoacetate. From their results, Baly and Desch put forward the idea that the presence of the bands should be ascribed to an oscillation between the enolic and ketonic forms; and that the rôle of the alkali is to increase the rate of change, that is, to increase the number of molecules in the state of change. They had observed that hydrochloric acid has not the same effect as alkali; and this they accounted for by stating that "hydrochloric acid should have an exactly opposite effect, owing to the restraining influence it is known to exert on certain of these changes."

With regard to the latter part of the subject, it is sufficient to point out that the work of Knorr (*Ber.*, 1911, **44**, 1150) on ethyl acetoacetate conclusively proves that both acids and bases have the same influence in the case of the transformation of the enolic into the ketonic form; so that the assumption made by Baly and Desch is unfounded.

Further, K. H. Meyer (*Annalen*, 1911, **380**, 212) has shown by purely chemical means that both enolic and ketonic forms of ethyl acetoacetate are present in ethyl-alcoholic solution; so that if Baly and Desch's views were correct, an absorption band should make its appearance in such a solution. No band, however, is observed under these conditions.

The cases of the hydrochloric acid solution and the solution of the pure ethyl acetoacetate having thus been disposed of, we come to the question of the bands produced in presence of alkali. Hantzsch (*loc. cit.*) has shown that if two solutions of ethyl acetoacetate in alcohol are taken, one of which is much more dilute than the other, it is necessary to add very much more alkali to the weak solution than to the more concentrated one in order to produce the same persistence in the band. This observation appears to dispose of any idea that the sodium ethoxide acts as a catalyst, and seems to point rather to the view that a hydrolysable salt is formed by the action of the alkali on the ethyl acetoacetate, this salt being more strongly decomposed at high dilutions, and hence requiring the addition of more alkali under these conditions in order to form the same amount of salt which is produced by less alkali in more highly concentrated solutions of the ester. Hantzsch suggests that the band produced by the addition of alkali is simply the spectrum of the alkali salt of ethyl acetoacetate, and this view is strengthened

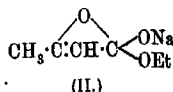
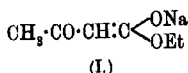
$N/100$ -methyl malonate is mixed with $N/100$ -sodium ethoxide; and it will be seen that the beginning of the band (incomplete) occurs at a much higher concentration than is the case when more sodium ethoxide is present. Now suppose that the band is the absorption spectrum of the sodium derivative. It is clear that when there is a high concentration of sodium ethoxide there will be a considerable percentage of sodium derivative present per c.c.; and hence the solution must be greatly diluted before the band is produced. On the other hand, when less sodium ethoxide is present, owing to hydrolysis, there will be less of the sodium derivative present per c.c., and hence a thicker layer of solution must be employed in order to get the same absorption. This agrees entirely with our results, as can be seen from the curves. Again, the dotted line shows the result of further dilution. It represents the spectrum of $N/1000$ -methyl malonate in the presence of $N/1000$ -sodium ethoxide. In this case the hydrolysis of the sodium derivative will be greater still than before; and consequently a c.c. of the solution will contain very little of it, and will therefore be very diacetic, as is shown in the curve.

We have spoken of the "hydrolysis" of the salt, although our results might be just as easily explained by considering the chances of the formation of the sodium derivative under the mass-action law. Our results in aqueous solution, however, seem to justify our assumption. Under these conditions, as is well known, sodium derivatives such as these are much more readily decomposed than when dissolved in alcohol. We must therefore assume that in aqueous solution hydrolysis will be greater than in alcoholic solution; consequently, in order to have a given amount of sodium derivative present it will be necessary to employ much more concentrated solutions here than is necessary to do in alcoholic solutions. The curves in Fig. 1 show that this is actually the experimental result. In alcohol with $N/10$ -sodium ethoxide present only a $N/10,000$ -solution is required to show the band; whilst in water with $N/10$ -sodium hydroxide present a $N/10$ -solution of the malonate in approximately the same thicknesses is needed.

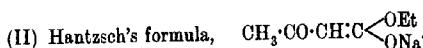
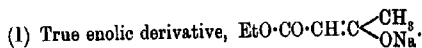
From these results, which agree with those obtained by Hantzsch in the case of ethyl acetoacetate, it seems evident that the band in these spectra has nothing whatever to do with the process suggested by Baly and Desch, but is merely due to the presence of the metallic derivative in solution.

We may now consider Hantzsch's views on this point. Since the enolic form of ethyl acetoacetate shows no band, whilst the sodium and aluminium derivatives manifest it, we are driven to conclude that there must be some constitutional difference between the enolic

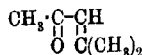
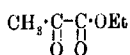
form and the sodium compound; for otherwise we should need to assume that two similarly constituted compounds have different spectra, which has not yet been found to be the case. Hantzsch examined two possible structures for the sodium derivative which are not derived from the true enolic form, and rejected the second



on the ground that it was too saturated a substance to show the great absorptive power exhibited by the sodium derivative of ethyl acetoacetate. The first formula he also rejected on the ground that it was almost identical (überaus ähnlich) with the normal enolic structure. A close examination will show that this is hardly justifiable without evidence. If we compare the two structures:



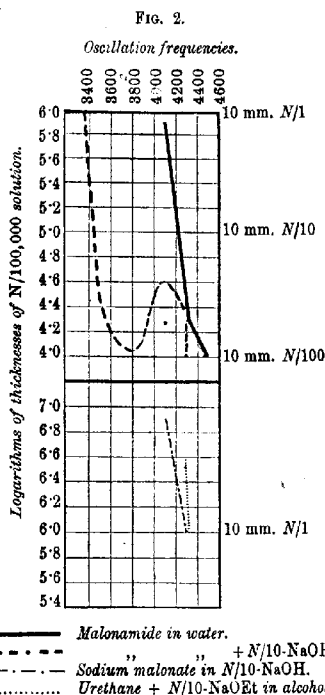
it will be seen that in the one case (II) there is a true carbonyl radicle, whilst in the other case (I) the carbonyl group of a carboxyl radicle is present, which shows no trace of carbonyl properties. It seemed quite possible that this difference might be sufficient to account for the difference in spectra; and we therefore endeavoured to find some compound containing the structure $\cdot \text{CO} \cdot \text{CH} : \text{C} \cdot$, which occurs in (II). The simplest substance appeared to be mesityl oxide, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH} : \text{C}(\text{CH}_3)_2$, so we examined the spectrum of this substance, which is shown in Fig. 3. It will be seen that the structure $\cdot \text{CO} \cdot \text{CH} : \text{C} \cdot$ does give rise to a band; but this band has its head at 3100, whereas the band in the spectrum of ethyl sodioacetoacetate occurs at 3700. On photographing mesityl oxide in the presence of alkali, we found that no change took place in its spectrum. This band in the mesityl oxide spectrum probably owes its appearance to a process similar to that which produces the band in the spectrum of ethyl pyruvate, as the two substances contain a similar system of double bonds:



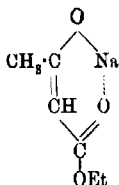
This is not an absolutely conclusive proof that the formula (II) above is not correct, but it seems sufficient.

We now come to Hantzsch's suggestion for a formula which differs sufficiently from the ordinary enolic form to account for the difference in spectra observed in practice. Hantzsch assumes that

the metallic derivatives of ethyl acetoacetate are derived from the enolic form, but differ from it in that the metallic atom is played upon by the residual affinity of the carbonyl radicle in such a way

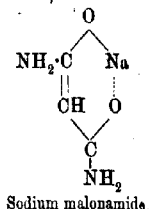
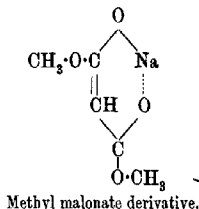


as to form an internal complex salt which may be represented thus:



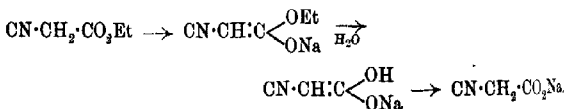
the dotted line showing the residual affinity's attraction. This view necessitates the formation of a six-membered "ring" in the molecule, and we have endeavoured to see whether it stands the test

in the malonic series as well as in the derivatives of ethyl acetoacetate. In the case of the sodium derivative of methyl malonate, the formation of the six-membered "ring" would be represented by the following formula:



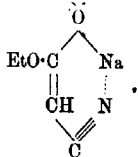
so that in this case the theory agrees with the facts. A similar "ring" might be produced in malonamide, which also shows an absorption band in the presence of alkali (see Fig. 2).

When ethyl cyanoacetate is considered, a reference to the curves in Fig. 3 will show that this substance behaves differently from those mentioned above. Instead of developing a band in the presence of sodium ethoxide, the compound shows only an increase in general absorptive power, although the rapid extension of its spectrum takes place in a region where the band occurs in the spectrum of methyl malonate in the presence of alkali. The curve of the absorption of ethyl cyanoacetate in aqueous solution shows but slight absorptive power, and no selective absorption is found when alkali is added to the solution. A consideration of the reactions of ethyl cyanoacetate throws some light on this abnormal behaviour. Although the substance is known to form a sodium derivative which can be obtained in alcoholic solution, this compound undergoes a peculiar decomposition in the presence of water, being converted into sodium cyanoacetate; and this change might best be accounted for by the following series of rearrangements:



If we were to assume the structure of the sodium derivative to be $\text{Na}\cdot\text{N}\cdot\text{C}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, the change from ester to salt could not be accounted for so simply. We may reasonably make the assumption that the structure of the sodium derivative is that shown in the first set of formulae, in which the sodium atom is attached to oxygen. If this be postulated, however, then the conditions necessary for Hantzsch's six-membered "ring" are not quite the same as in the

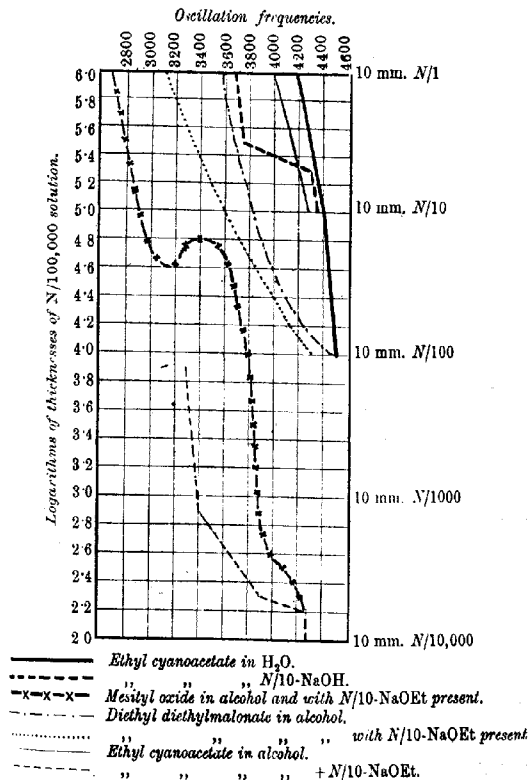
previous cases, as there is no carbonyl radicle to attract the sodium atom, but instead of it we have the $\cdot\text{CN}$ group:



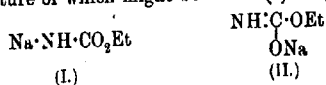
This difference in the groups might very well be sufficient to produce an abnormality in the absorption spectrum; and thus the case rather strengthens Hantzsch's arguments.

We endeavoured to find another example of the same type, and

FIG. 3.



examined malonitrile. Unfortunately, this compound proved to be so readily oxidised, especially in the presence of alkali, that no trustworthy results could be obtained from it. We next photographed the spectrum of urethane, which yields a sodium derivative the structure of which might be either (I) or (II):

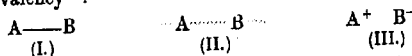


In neither case is the formation of Hantzsch's six-membered "ring" possible, and as can be seen from the curve in Fig. 2 this body is very feebly absorbent, even in presence of sodium ethoxide.

The foregoing evidence appears to confirm the view that the bands in the spectra of substances capable of yielding a sodium derivative are due to the formation of an internal salt. The formation of the simple sodium salt alone is insufficient, as otherwise urethane and ethyl cyanoacetate would show bands in their spectra when photographed in the presence of sodium ethoxide. It therefore seems clear that Hantzsch's theory is correct, and that the previous attempt at the solution of the problem must be ruled out of account.

The assumption of the existence of the internal salt formation, however, does not carry us sufficiently far. It fails to account for the difference between the spectra of the enolic form of ethyl acetoacetate and the sodium derivative; for if it is to be assumed that sodium has an auxiliary valency, it will be illogical to refuse one to the hydrogen atom. Also, we must account for the fact that whilst ethyl β -chlorocrotonate shows no band in its spectrum, ethyl β -aminocrotonate* has a band in exactly the same position as that due to the sodium salt of ethyl acetoacetate. This difficulty disappears if we take into account the theory of valency recently put forward by Gebhard (*J. pr. Chem.*, 1911, [ii], 84, 561).

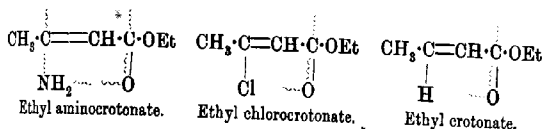
According to Gebhard, when two atoms are united together directly by their maximum valency, the result can be represented as in (I) below. Now if any weakening in the bond between A and B takes place, the total amount of affinity of the two atoms is unaltered in quantity, so that the residual affinity must make its appearance on the two atoms as free affinity. This can be represented as in (II), and such a bond is termed by Gebhard an "ionised valency":



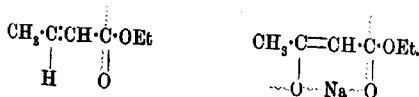
* The curves given by Baly and Desch (*T.*, 1904, 85, 1089) appear to be incorrectly numbered. We have photographed the spectrum of ethyl β -aminocrotonate and find that it is similar to curve 1 on the figure, not curve 3. It appears that the numbering of the curves has been inverted.

Case (III) represents the extreme state of dissociation, where the two atoms have separated from each other.

Now applying this idea to the case of ethyl β -aminocrotonate, the following result is obtained. It is well-established that the amino-group is very loosely held to the carbon, since it can be eliminated with great ease. This union should therefore be represented as being weaker than the full affinity of a single bond, and, consequently, we are led to postulate a superfluity of free affinity on the amino-group. This free affinity being in the 1:5-position with regard to the unsaturated carbonyl oxygen of the carboxyl group, will tend to interfere with the latter, and to this interaction of the two residual affinities we trace the origin of the band in the spectrum of the substance. In the case of ethyl β -chlorocrotonate the chlorine atom is by no means so labile as the amino-group in the amino-ester, so that we are justified in concluding that it is bound to the carbon by an ordinary unweakened bond. There will therefore be little free affinity on the chlorine, and hence there will be no play of unsaturations such as occurs in the other case. The same reasoning gives the clue to the absence of a band from the spectrum of ethyl crotonate itself:



Similar reasoning applies in the case of the enolic form of ethyl acetoacetate and its sodium derivative. In the enolic modification, since there is very slight ionisation, we are entitled to assume that the union between the hydrogen and oxygen atoms of the hydroxyl group is a strong one; but in the case of the sodium salt, which is much more readily dissociated, it must be assumed that this union is weaker. This would be represented in the two cases, as shown below, and it will be seen that the result in the one case is a more or less saturated hydrogen atom, whilst in the latter example there is an accumulation of free affinity on the sodium; so that the sodium salt gives results parallel with those obtained from ethyl aminocrotonate:

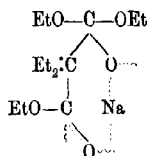


Thus we have a more or less clear expression of these differences, and the hypothesis appears to account for the salient facts, whilst it differs from Hantzsch's views only to the extent of the difference

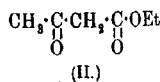
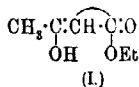
in interpretation of the state of affairs in the relations between the sodium atom and the carbonyl group.

One or two other points of interest have come to light in the course of this investigation. On examining the absorption spectrum of sodium malonate in alkaline solution, no band could be detected (see Fig. 2). This may be accounted for if we assume that the sodium derivative of sodium malonate is extremely easily hydrolysed by water.

On examining the spectrum of ethyl diethylmalonate (Fig. 3) we found that a considerable increase in the general absorption takes place on the addition of alkali to the solution. This might be accounted for by assuming some sort of space-conjugation between the carbonyl groups under the influence of the alkali, since these groups are in the critical 1:5-position with regard to one another. Or it might be explained by assuming the formation of an additive compound somewhat similar to those formulated by Gebhard (*loc. cit.*) in the case of the hydrochloride of benzo-pinacolin:



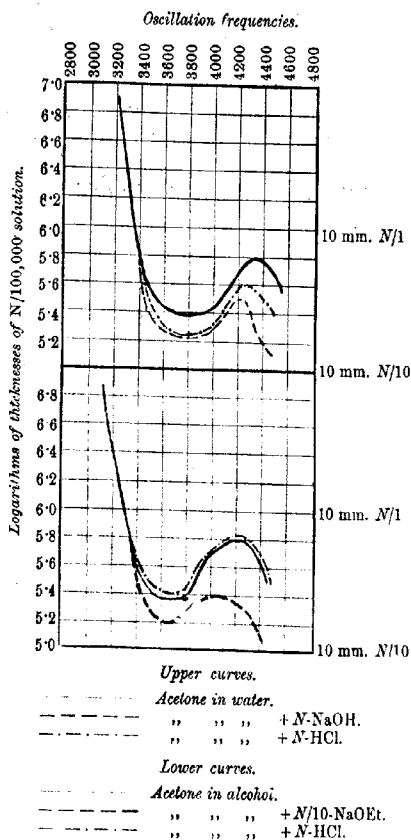
Turning to the action of hydrochloric acid on compounds containing a labile hydrogen atom, we have noticed a point which seems worth mentioning. Baly and Desch (*loc. cit.*) observed that the addition of hydrochloric acid rendered ethyl acetoacetate much more diactinic. On repeating this experiment with methyl malonate we found that the presence of hydrochloric acid made practically no difference to the spectrum of this substance. Now when the grouping (I), enolic form, is converted into (II), ketonic form, it will be seen that there is a decrease in the conjugation within the molecule; enolic ethyl acetoacetate contains two conjugated double bonds which are unconjugated in the ketonic substance:



Hence it follows (Crymble, Stewart, Wright, and Glendinning T., 1911, 99, 451; Crymble, Stewart, Wright, and Miss Rea, *ibid.* p. 1262) that the ketonic form will be the more diactinic of the two; and that the change from the enolic to the ketonic form will

be accompanied by a decrease in absorptive power. Now K. H. Meyer (*Ber.*, 1912, **45**, 2846) has shown that ethyl acetoacetate in alcoholic solution contains 12.7 per cent. of the enolic form, which, being pseudo-acidic, will be converted into the ketonic form by the

FIG. 4.



action of mineral acid. On the other hand, methyl malonate contains no enolic form under the same conditions, so that hydrochloric acid cannot have any influence in its case, which agrees with the spectroscopic results.

Finally, we come to a point which seems to be of some import-

ance. It has been mentioned in the course of this paper that we tried the effect of adding alkali to a solution of mesityl oxide, but found that it produced no change in the substance's absorptive power. We have applied this test to several other substances, and have found that no marked change in their bands is produced by alkali. In the case of acetone* the amount of change produced either by acid or by alkali is almost within the limit of experimental error (see Fig. 4; the differences have been very slightly exaggerated to make the drawings clearer). This at once suggests that we have a test by which we may differentiate between different types of absorption, and we propose to continue this work immediately. It is possible that the differentiation may be found only in cases in which we are concerned with a hydrogen atom replaceable by metals, and if this were so, the method would not be of much interest; but the case of ethyl diethylmalonate mentioned above seems to point to the possibility of the influence of alkali being traceable even when no replaceable hydrogen atom is present. Hitherto it has been customary to assume that when two bands occurred at the same frequency, they owed their origin to analogous causes; but if it could be proved that the action of sodium or acid yielded different results in the two cases, this view would fall to the ground, and we should have a means of classifying bands much more accurately than any at present at our disposal.

Summary.

(1) Various compounds containing labile hydrogen atoms have been examined, and it was found that these may be divided into two classes, namely, (i) those which, showing only general absorption in alcoholic solution, give rise to banded absorption in presence of alkali, and (ii) those which do not conform to this rule even when the sodium derivative is an isolable substance.

(2) In the case of those substance which develop a band in their spectrum in the presence of alkali it was shown that the persistence of the bands depends on the relative quantities of alkali present. This had already been shown by Hantzsch in the case of ethyl acetoacetate, and our work lends additional support to his view that the bands are merely the spectra of the alkali salts of these compounds containing the group $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot$.

(3) The alkali salt alone does not necessarily give rise to the band, but in those cases where the formation of internal complex

* The curve for acetone in aqueous solution given in T., 1906, 87, 492 seems to be incorrect. It was obtained with a spectrograph much inferior to the one now used by us and the error may be due to this cause (see Baly, T., 1910, 97, 571 for a similar error in the case of nitrobenzene).

alts (or where there is a spatial possibility of mutual influence of free affinity) we have found a band in the spectrum; whereas in other cases where such conditions do not obtain we have not observed the production of any band.

(4) This work, which forms an extension of Hantzsch's, conclusively disproves the explanation put forward by Baly and Desch to account for these bands.

In conclusion, we desire to express our thanks to Professor Letts and Prof. Inglis for the interest they have taken in the work.

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XLIX.—*The Presence of Neon in Hydrogen after the Passage of the Electric Discharge through the latter at Low Pressures.*

By JOHN NORMAN COLLIE and HUBERT SUTTON PATTERSON.

THIS communication has been divided into two parts for the following reason. In the early portion of the work neither of the authors was aware of the work of the other, and it was not until the later stages that they had learnt that they were getting the same results independently; it seemed best therefore to collaborate and publish the work in a joint paper. Also, as both the authors had approached the problem from different points of view, it is better to keep the early results separate, in order to show how the two lines of research came together.

PART I (By J. N. COLLIE).

A good many years ago the author had noticed that many minerals change colour when bombarded by cathode rays, notably sodalite and fluorspar. At the same time much gas is given off. It was partly to investigate this change of colour, and partly to investigate the nature of the evolved gases, that from time to time various substances were subjected in tubes at low pressure to the action of high voltage electricity. In a letter to *Nature* last July (89, 502), Sir William Ramsay mentioned that the author had noticed that neon was present in the gas emitted from calcium fluoride when under the action of cathode rays. Both natural fluorspar, and calcium fluoride made by allowing hydrofluoric acid to act on lime, change colour when bombarded by cathode rays.

The substance becomes first pink, then purple, and in the case of crystals of fluorspar the surface becomes a deep purple, with a metallic, copper-coloured reflection. The action is only a surface one, and is probably due to metallic calcium, for if the purple substance is put into red litmus paper with some water the litmus becomes blue, and the purple compound disappears. The action of the cathode rays is therefore a powerful one, and if metallic calcium is set free, fluorine should be liberated as well. A small vacuum tube on the apparatus, however, gave no spectrum of fluorine, but only that of hydrogen and carbon gases. With the spark from a Leyden jar, silicon fluoride could be detected, and oxygen was also found in the gases, but this may have been formed by decomposition of water vapour.

It was found to be excessively difficult to get calcium fluoride in a condition so as to give no gas when bombarded by cathode rays. To give one experiment: Pure, fresh lime from marble was treated in a platinum basin with pure hydrofluoric acid in excess and evaporated to dryness. Again it was moistened with hydrofluoric acid, evaporated, and heated for a couple of hours in a muffle furnace to a temperature just short of fusion of the fluoride. As soon as cold it was put into a tube, in which it could be subjected to the cathode discharge. This tube had been carefully cleaned. After pumping out almost all the air from tube, the current was turned on, and gas at once began to come off the fluoride. By heating the fluoride with a bunsen burner, more gas came off, the gas being, as far as one could tell from the spectrum, a mixture of hydrogen and carbon monoxide. This evolution of gas from what was presumably pure calcium fluoride continued for about a week, the fluoride being bombarded by cathode rays and being heated for about six hours a day. During that time between 3 and 4 c.c. of gas were pumped off. Finally the tube ceased working, and no heating or bombardment by means of cathode rays liberated any more gas.

As this gas consisted almost entirely of carbon monoxide, hydrogen, oxygen, and a trace of silicon fluoride, these gases had presumably been formed from the calcium fluoride, water, and carbonaceous material in the tube; and the author has found that to get a tube that will not give carbon gases when it is violently heated and subjected at the same time to cathode discharge is a very difficult task.

The above mixture of gases were sparked, then treated with liquid air and charcoal, and the residue forced up into a capillary tube, where its spectrum could be obtained. This residue contained neon. This result being so extraordinary, further experiments were

made. The length of the bombardment during the experiments was, as a rule, from three to six hours.

Experiment 1.—The calcium fluoride was replaced by some ten years old glass wool that had been carefully cleaned with sulphuric acid and chromic acid. The glass was dried at 120°. On bombarding with cathode rays, quantities of water vapour were evolved, and later carbon gases. These gases contained neon.

Experiment 2.—The glass wool was taken out of the tube, and in order that the current should pass at low pressures 3–4 c.c. of pure hydrogen were admitted little by little, and pumped off. The tube was heated during the experiment. The hydrogen was exploded with excess of pure oxygen, and the oxygen finally removed by charcoal cooled by liquid air. Neon was found.

It was then obvious that either the neon was being formed in the tube during the experiment, or that in some way air had leaked into the tube or the pump during the experiment. That air had not leaked into the pump was rendered highly improbable, for always at the end of a day's experiments a phosphorescent vacuum was left in the tube, and no change was found on examining the apparatus on the next day or the next but one. Moreover, a vacuum tube was in connexion with the tube, and the minutest trace of air would have meant a spectrum of nitrogen in the vacuum tube.

Experiment 3.—A tube was run intermittently for four days, and neon was found to be present. The oxygen gas that had been absorbed by the charcoal was collected, and put into a tube over mercury with phosphorus. All except a bubble the size of a large pin's head was absorbed. The amount of neon obtained in the experiment was about the same amount that was left when 1–2 c.c. of air were treated with cooled charcoal.* That would mean at least 1.0 c.c. of residual nitrogen if the neon found was due to an air leak. The pin's head of gas that remained over was found, however, when examined in a spectrum tube, to be pure hydrogen, and not nitrogen.

From time to time blank experiments were made with larger quantities of the oxygen † and hydrogen used; they were twice put through the pump in exactly the same way as during an experiment, and larger quantities than were used during an experiment were exploded and the residue tested. In no case was neon found.

Experiment 4.—A glass balloon was sealed on to the pump instead

* The neon obtained in all these experiments may have contained helium, but if the latter gas were present it was there in very small quantities. What was taken for the yellow helium line was only seen occasionally.

† The oxygen was prepared by heating potassium permanganate, and the hydrogen by the action of sodium amalgam on boiled water.

of the ordinary tube. This was exhausted and heated for two days to such a temperature that part of the bottom slightly collapsed. Some pure oxygen was then admitted to wash out any gas in the balloon. When tested for neon, none was found. This experiment shows that neon is not evolved from the glass by heating alone; moreover, glass heated to near its softening point is not a porous membrane to atmospheric neon or helium. Later a considerable amount of the same glass as that used during these experiments was pounded up, cleaned with chromic and sulphuric acids, and heated until it fused in a hard glass tube. The gas evolved was examined and contained no neon.

Experiments were also made to see whether the neon came from the aluminium electrodes that were always used.

A tube was made so that the negative electrode could be fused up in a small glass cup by means of an extra powerful discharge. This was done, and the gas evolved was examined. It contained hydrogen, for it could be exploded with oxygen, but the residue contained no neon. Later a much larger amount of the aluminium wire used in the experiments was fused by heating with a bunsen burner in a hard glass tube. Some hydrogen was evolved, but it did not contain neon.

There still remained a possibility, although glass was not porous to neon when heated (compare experiment 4), that it might be so when subjected to a cathode discharge.

Experiment 5.—A tube was made so that the end containing the negative electrode was surrounded by another that could be worked from a separate pump. Into the outer tube pure neon was admitted up to a pressure of half an atmosphere. After running the tube for six hours the gas in the inner tube contained neon as usual, and in about the same amount.

Experiment 6.—The neon was pumped out of the outer tube, and helium substituted instead; during four days' working the tube not a trace of helium could be found in the inner tube, but there was the usual amount of neon.

Experiment 7.—Another tube was then made so that the whole of the inner tube was contained in an outer one. After working it for two days with such a vacuum in the outer tube that the spark would not pass through it, and having hydrogen in the inner tube, the gases of the inner tube were examined, and found to contain the usual amount of neon. Merely for curiosity, a c.c. of oxygen was admitted into the outer tube and pumped out. It gave a very faint explosion (hydrogen) when a spark was passed through it in an eudiometer. The residual oxygen was then treated with cooled charcoal. The residue that remained was about fifty

times as great as the residue from the inner tube, and when examined it was *mostly helium, with enough neon present to give the neon spectrum.*

Besides the above experiments many more were made, in all, thirty-five, and neon was found in greater or less quantity every time. Several times the lines were measured, and the following lines identified:

6678.50	6599.18	6506.69	6402.43
6383.14	6384.65	6163.73	6143.31
5096.36	6074.51	6030.20	5975.76
5882.06	5852.62		

All the apparatus was made by the author, and all the electrodes were made from fresh aluminium wire, and had not been used for any other purpose.

PART II (By H. S. PATTERSON).

This investigation was undertaken with the object of endeavouring to verify certain deductions from the formula for electronic mass:

$$m = \frac{2}{3} \frac{e^2}{a}.$$

a = radius of electron supposed spherical.

e = electric charge.

m = mass.

If the chief part of the mass of an atom be supposed to be due to a similar cause to that of an electron, that is, if m be the mass of an atom, a the radius of the sphere which is the seat of the major part of the mass, and e the charge on this sphere, then a becomes very much smaller than the radius of an atom as measured by other methods. This does not cause difficulty, since the radius of an atom as measured directly depends on the nearness of approach of one atom to another, whilst a is the radius of that part of the atom which is the seat of the major part of the mass. Suppose the α -particle and the hydrogen ion be considered; then, since the electric charge on the α -particle is twice that on the hydrogen ion, whilst their masses are in the ratio of 4 to 1, it follows that the radius of the seat of the major part of the mass of an atom may be the same in each case. If, therefore, by means of the electric discharge a second electric charge could be given to the seat of mass of the hydrogen ion, an α -particle might be produced, in which case it would be possible to convert a hydrogen atom into one of helium.

One way of attempting to verify these deductions seemed to be to subject hydrogen at a low pressure to the electric discharge, and,

after removing the excess of hydrogen, to examine the residue in a small spectrum tube.

The experiments were carried out in the following way. Hydrogen was prepared in an air-tight vessel by the electrolysis of a solution of barium hydroxide, boiled to free from air. The solution was purified from dissolved air finally, first by heating and passing through it about two litres of oxygen from a tube of potassium permanganate, which was then sealed off, and then by passing the current for some considerable time, when the solution became heated almost to boiling point, and allowing the electrolytic gas to escape. After these precautions, hydrogen, thus as completely as possible freed from air, was obtained on electrolysis, and after being dried over phosphoric oxide was let into a large Plücker tube with aluminium electrodes. The pressure in the discharge tube was at first about 2 mm., but was gradually reduced by an Antropoff pump to the point at which the discharge would only pass with great difficulty, the tube showing green phosphorescence. The process required in general about eight hours, the direction of the discharge being frequently reversed to get rid of any gas from the electrodes, and the discharge tube being continuously heated to obtain any gas driven into the glass. This was repeated until sufficient hydrogen, in some cases 30 c.c., had been treated. To the hydrogen which had been collected in an explosion tube was now added oxygen prepared from a potassium permanganate tube fixed on to the pump. After explosion of the hydrogen with excess of oxygen, the residue, consisting usually of about 0.1 c.c., and showing only the spectrum of oxygen, was taken into an apparatus in which the excess of oxygen could be removed by a charcoal bulb immersed in liquid air, whilst the gas remaining could be examined in a small spectrum tube. It was found that in fifteen experiments in which hydrogen was treated in this manner the spectrum of the final residue showed the presence of a quantity of neon. In four cases it was also possible to see faint traces of the spectrum of helium, but the spectrum of neon always very largely predominated.

To test the purity of the gases used, before each experiment a similar volume of hydrogen was treated in exactly the same way as before, but the discharge at low pressures was not passed. Under these conditions not the slightest trace of helium or neon could be detected. If even 200 c.c. of hydrogen were treated without passing the discharge, no helium or neon could be found. The oxygen was also treated in quantities both similar to and much greater than were used, by adsorption with charcoal cooled by liquid air, and examination for any residue. It was found, however, that not a trace of helium or neon could be seen. In all cases before an

experiment the discharge tube was heated and exhausted until the discharge would only pass with great difficulty, and throughout the experiments the discharge tube was never open to the air. The aluminium of the electrodes was tested by melting in a vacuum, then washing out the tube with oxygen, and absorbing the oxygen by charcoal and examining the residue. Under these conditions not a trace of helium or neon was found.

With regard to the quantities of neon produced, it was found that from about 20 c.c. of hydrogen treated as above, the neon obtained was equivalent approximately to that occurring in 1 c.c. of air. The helium, however, was much less, for whilst in 1 c.c. of air the helium can be readily detected spectroscopically, in the experiments described the helium only occurred in such small quantities as to be almost invisible. It is noteworthy that on account of the adsorption of neon by charcoal, the tendency would be to increase the percentage of helium in the spectrum tube.

After hearing of Professor Collie's experiments with a jacketed cathode, experiments were made in double-walled discharge tubes. Hydrogen was put into the inner tube, in which were aluminium electrodes, and the experiment performed as before, the outer tube being exhausted so that the discharge would not pass. Under these conditions, neon, with a trace of helium, was found in the inner tube. Information having been received from Professor Collie that he had obtained large quantities of helium with some neon from the outer tube, this gas was looked for by washing out the outer tube with 1 c.c. of oxygen and absorbing the oxygen by charcoal cooled by liquid air. It was then found, in agreement with Professor Collie's results, that the residue consisted spectroscopically largely of helium mixed with a little neon. Another experiment was now made in which pure oxygen at a pressure of about 15 mm. was put into the outer tube, the inner tube containing hydrogen originally at a pressure of about 2 mm. On performing an experiment with the hydrogen in the inner tube as before, it was found that the residual gas in the inner tube consisted of neon. The major part of the oxygen in the outer tube was now removed by charcoal, the last 2 or 3 c.c. pumped out, and, after adsorption of the remaining oxygen, examined in a small spectrum tube. A residue was found which appeared spectroscopically to consist of almost pure neon with a little helium. In each of these last two experiments, the residue consisted of about a cu. mm. of gas, in the first case largely helium, in the second, largely neon.

Conclusion.

Whatever the explanation of the above results may be, the facts seem to be the following:

1. Neon cannot be obtained from either the glass or the electrodes by heating alone.
2. The neon found is not due to air leaking into the pump or the apparatus during the experiment.
3. Glass, neither when heated to near its softening point, nor under the action of cathode rays, is permeable to ordinary neon or helium.
4. The hydrogen and the oxygen used in the experiments did not contain neon.

Moreover, the appearance of helium and neon in the outer tube as well as neon in the inner tube is most important. It would appear impossible that particles of these gases are shot through the glass from the inner to the outer tube; the question obviously is where do these gases come from? The answer to that question cannot at present be given with any certainty, but it is hoped that this line of research may ultimately throw more light on the subject. Since this paper was read Sir J. J. Thomson, in a letter to *Nature* (90, 645) gives an account of some experiments he has been making that have a direct bearing on the phenomena in question.

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L.—*The Double Platinic and Cupric Iodides of
Substituted Ammonium Bases.*

By RASIK LAL DATTA.

The Double Platinic Iodides.

THE double platinic iodides of the alkali and alkaline earth metals were first prepared by Lassaigne (*Annalen*, 1833, **8**, 185) by dissolving platinic iodide in solutions of the respective metallic iodides. Later, Mather and Platt (*Amer. Chem. J.*, 1834, **27**, 257) prepared potassium platini-iodide by mixing a solution of platinic chloride with a slight excess of potassium iodide, evaporating to dryness on the water-bath, and extracting with a mixture of alcohol and ether so long as the colour was communicated to the washing liquid. It is evident that Mather and Platt obtained the compound in a

highly impure state, largely contaminated with potassium chloride, since by this interaction much potassium chloride is formed which cannot entirely be washed out by the solvent used by them.

Kane (*Phil. Mag.*, 1833, 2, 198) attempted to prepare ammonium and potassium platini-iodides by treating pulverised potassium iodide and ammonium iodide respectively with platinic chloride solution and washing the precipitates obtained with ether. His method, however, did not lead to the preparation of pure compounds, and he necessarily failed to arrive at a definite conclusion.

The following double iodides have been directly obtained as black, crystalline precipitates by adding platinic chloride to solutions of alkali and substituted ammonium iodides, but it has been found that double platinic iodides of sodium and alkaline earth metals could not be precipitated similarly owing to their extreme solubility.

Rubidium Platini-iodide.

This salt is not so soluble as the potassium salt, as was to be expected from a comparison of the solubility of the platini-chlorides. Hence it was obtained from a tolerably concentrated solution as a black, crystalline precipitate. It is moderately soluble in water:

0.3321 gave 0.4884 AgI. $I = 67.73$.

Rb_3PtI_6 requires $I = 67.55$ per cent.

Caesium Platini-iodide.

This is a sparingly soluble salt, and was obtained by precipitation of dilute solutions:

0.1037 gave 0.1251 AgI. $I = 62.99$.

Cs_3PtI_6 requires $I = 62.36$ per cent.

It is a black powder, only sparingly soluble in water, forming a faintly-coloured solution. Its sparing solubility is quite in keeping with the intense electropositiveness of the metal, and it is one of the most stable platini-iodides.

Methylammonium Platini-iodide.

This was obtained as a black precipitate, which was washed and dried in the desiccator over sulphuric acid:

0.2239 gave 0.0424 Pt. $Pt = 18.92$.

0.1021 „ 0.1416 AgI. $I = 74.96$.

$2CH_3N, H_2PtI_6$ requires $Pt = 19.09$; $I = 74.63$ per cent.

This salt is freely soluble in water, but less so than the corresponding salt with ammonium iodide, forming a deep red solution.

As a general rule it may be laid down that the solubility is dependent on the weight of the ammonium base, salts with the quaternary bases being the least soluble. This salt is sparingly soluble in a mixture of alcohol and ether, from which it may be crystallised.

Ethylammonium Platini-iodide.

This compound is obtained as a crystalline, black precipitate soluble in water to a red solution. It was dried in the desiccator over sulphuric acid:

0.2132 gave 0.0400 Pt. Pt=18.76.

$2C_2H_7N, H_2PtI_6$ requires Pt=18.59 per cent.

Allylammonium Platini-iodide.

To a concentrated solution of allylammonium iodide a 10 per cent. solution of platinic chloride was added; the solution became dark red, and in a few seconds a mass of slender crystals precipitated. These were collected, washed with a little water, and dried in the desiccator:

0.1044 gave 0.0189 Pt. Pt=18.10.

$2C_3H_7N, H_2PtI_6$ requires Pt=18.17 per cent.

Anilinium Platini-iodide.

This is obtained as a black powder moderately soluble in water, giving a dark red solution:

0.2879 gave 0.0493 Pt. Pt=17.13.

$2C_6H_7N, H_2PtI_6$ requires Pt=17.06 per cent.

Dimethylammonium Platini-iodide.

The compound is a black powder, soluble in water to a red solution. The solubility of this iodide is less than the primary ammonium platini-iodides:

0.2611 gave 0.0488 Pt. Pt=18.69.

0.1037 „ 0.1368 AgI. I=72.27.

$2C_2H_7N, H_2PtI_6$ requires Pt=18.59; I=72.64 per cent.

Diethylammonium Platini-iodide.

The compound was obtained as a black precipitate:

0.2035 gave 0.0361 Pt. Pt=17.74.

$2C_4H_{11}N, H_2PtI_6$ requires Pt=17.64 per cent.

Trimethylammonium Platini-iodide.

This compound is obtained as a black precipitate from moderately dilute solution:

0.2016 gave 0.0368 Pt. Pt=18.25.

0.0936 „ 0.1218 AgI. I=70.32.

$2C_3H_9N, H_2PtI_6$ requires Pt=18.10; I=70.75 per cent.

Triethylammonium Platini-iodide.

This is a black powder, sparingly soluble in water:

0.2139 gave 0.0364 Pt. Pt=17.01.

$2C_6H_{15}N, H_2PtI_6$ requires Pt=16.88 per cent.

Tetramethylammonium Platini-iodide.

Tetramethylammonium iodide is generally prepared by heating methyl iodide with alcoholic ammonia in a sealed tube. It was, however, obtained rapidly, and in a very short time by shaking in a stout, stoppered bottle a mixture of methyl iodide, aqueous ammonia, and methyl alcohol, the latter being added to facilitate the mixing of the iodide with aqueous ammonia. Heat was gradually developed, and a homogeneous mixture was obtained with the deposition of a fine, crystalline powder. By the time the bottle cooled, the deposition was complete. The crystals were washed with methyl alcohol and dried. The purity of the sample was ascertained by an iodine estimation. (Found, I=63.12. Calc., I=63.18 per cent.)

The double iodide was obtained as a black precipitate from moderately dilute solutions. It is sparingly soluble in water, giving a wine-red solution:

0.2677 gave 0.0472 Pt. Pt=17.62.

$2C_4H_{12}NI, PtI_4$ requires Pt=17.64 per cent.

Tetraethylammonium Platini-iodide.

Unlike the compound just described, this has a red colour, and is very sparingly soluble in water:

0.2810 gave 0.0456 Pt. Pt=16.23.

$2C_6H_{18}NI, PtI_4$ requires Pt=16.02 per cent.

Pyridinium Platini-iodide.

This compound is precipitated on adding platinic chloride to a dilute solution of pyridine hydriodide. The substance was obtained in an extremely fine state of division, and was difficult to wash.

VOL. CIII.

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The salt was dried as usual, and had a red tinge similar to that of the preceding compound. This red tinge may be characteristic of very heavily substituted ammonium bases, since it is absent in the case of the lower members:

0.2065 gave 0.0365 Pt. Pt = 17.63.

$2C_6H_5N_3H_2PtI_6$ requires Pt = 17.47 per cent.

The reaction exemplified above may be used as a convenient analytical method for controlling the purity and composition of bases which are directly obtainable from reaction mixtures as iodides. Hitherto such iodides had to be converted into the chlorides through the hydroxides, and finally the platinichloride had to be prepared. It is, however, unnecessary to convert the iodide into its chloride, it being only requisite to add platonic chloride to the iodide solution direct, and to estimate platinum in the precipitated salt.

It may be pointed out that Peterson (*Zeitsch. anorg. Chem.*, 1898, **19**, 59), in describing the volumetric estimation of platinum, mentioned that platonic iodide is unstable, decomposing into platinous iodide and iodine. It is evident, however, from the isolation of platonic iodide itself by Lassaigne that Peterson's view as to the decomposability of platonic iodide is incorrect, and he was led to this conclusion by the fact that the reddish-brown solution can be titrated with thiosulphate. The titration becomes possible by the fact that sodium thiosulphate decomposes platonic iodide itself in combination with alkali and ammonium iodides.

The Double Cupric Iodides.

By adding cupric chloride to solutions of the substituted ammonium iodides, a series of double salts with cupric iodide has been obtained. These double iodides are, however, highly unstable, and can only be prepared with difficulty, since they are readily decomposable by water into cuprous iodide, iodine, and the respective ammonium iodide. In this reaction the cupric iodide which is liberated in the presence of a large excess of substituted ammonium iodide finds a favourable opportunity of combining with the latter, and precipitates as an ammonium cupri-iodide. It is, in fact, the simultaneous combination with substituted ammonium iodides during the liberation of cupric iodide in the nascent state that makes the existence of these double cupric iodides possible, the ammonium iodides contributing materially to their formation by reason of their affinity towards iodine.

The formation of double cupric iodides with alkali metals and ammonia has been found to fail, the reaction taking the usual

course. Iodides of ammonium bases which are heavily substituted, yield these double iodides with great facility. It is to be noticed that the more heavily the ammonium base is substituted the more stable is the double cupric iodide obtained with it. With those ammonium bases which are very lightly substituted, the double iodides could not be formed at all. With tolerably heavily substituted bases, the formation is somewhat difficult, and saturated solutions of the ammonium iodide must be used, since the double salt is decomposable by water, and might be precipitated in a decomposed state, mixed with free iodine; for instance, when a concentrated solution of cupric chloride is added to an excess of a saturated solution of tetraethylammonium iodide, a brick-red precipitate is obtained, which, when washed with water, decomposes, evidently owing to the decomposition of combined cupric iodide into cuprous iodide and iodine, which latter imparts a black colour to the precipitate. This behaviour is common to nearly all double iodides of this series, but there is a difference in the degree of decomposition depending on the weight of the base. In the same way, pyridinium iodide gives a salt which cannot be washed without turning black, and the salt with quinolinium iodide behaves similarly. It is interesting to note that these salts during their decomposition by water lose their crystalline shape, the whole congealing to a black, plastic mass. Tetrapropylammonium cupri-iodide has been found to be the most stable of all the double iodides that have been hitherto prepared, so much so that it can be washed freely with water, and remains undecomposed even when treated with large quantities of water.

It has to be noted that two series of salts have been obtained; for example, with tetraethylammonium iodide, as also with pyridinium or quinolinium iodide, salts of the type $2NR_4I$, CuI_2 , or $(NR_4)_2CuI_4$ are formed; but with tetrapropylammonium iodide a salt of the type NR_4I , CuI_2 , or NR_4CuI_3 is formed.

Tetraethylammonium Cupri-iodide.

This was obtained as a brown precipitate by adding a concentrated solution of cupric chloride to a concentrated solution of tetraethylammonium iodide. It is important to note that during the washing of the salt the upper layer suddenly turns black, owing to the decomposition of the salt as mentioned above. However, the decomposition was avoided by using a small quantity of water:

0.2031 gave 0.0178 CuO . $Cu = 7.00$.

$2C_8H_{20}NI, CuI_2$ requires $Cu = 7.58$ per cent.

Tetrapropylammonium Cupri-iodide.

This compound was obtained as a brick-red precipitate, which was washed with water, and dried in the desiccator. The salt is fairly stable, and can be washed freely without being decomposed. It has the formula $N(C_3H_7)_4I, CuI_2$:

0.2238 gave 0.0276 CuO. Cu = 9.86.

$C_{12}H_{28}NI, CuI_2$ requires Cu = 10.12 per cent.

Pyridinium Cupri-iodide.

This salt was obtained by precipitating a concentrated solution of pyridine hydriodide by cupric chloride. It was collected by the aid of the pump so as to free it from the adhering mother liquor as far as practicable. The salt could not be washed, since the addition of only a small quantity of water has the effect of blackening, and hence decomposing the salt:

0.2512 gave 0.0249 CuO. Cu = 7.92.

$2C_5H_5N, 2HI, CuI_2$ requires Cu = 8.62 per cent.

Quinolinium Cupri-iodide.

This was obtained as a brick-red precipitate by the usual method. It cannot be washed for reasons previously indicated, and when added to a large volume of water, turns black, and its crystalline shape is lost, the whole congealing to a black, plastic mass:

0.2819 gave 0.0252 CuO. Cu = 7.14.

0.3215 „ 0.0289 Cu_2S . Cu = 7.18.

$2C_9H_7N, 2HI, CuI_2$ requires Cu = 7.58 per cent.

The low percentage of copper in the above salts is due to the impossibility of washing the salt free from the adhering ammonium iodides.

I take the opportunity to express my best thanks to Prof. P. C. Rây for his encouragement in carrying on the above investigation.

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LI.—*The Absorption Spectra of Simple Aliphatic Substances in Solutions and as Vapours. Part II. Unsaturated Aldehydes and Ketones.*

By JOHN EDWARD PURVIS and NIAL PATRICK MCCLELAND.

IN a previous communication (T., 1912, 101, 1810) the authors have given an account of the absorption spectra of various saturated aliphatic aldehydes and ketones in solutions, vapours, and thin films.

The aim of the present paper is to describe a series of observations of the absorption spectra in the ultra-violet regions of various unsaturated aldehydes and ketones when in solution and as vapours, and to compare them with several of their corresponding alcohol and acid derivatives.

The following substances were examined: acraldehyde, crotonaldehyde, citral, allylacetone, methyl allyl ketone, methyl propenyl ketone, mesityl oxide, phorone, allyl alcohol, allyl bromide, and crotonic acid.

The experimental methods have been described before. The substances were obtained by methods which are well known, with the exception, perhaps, of methyl allyl ketone, and this was prepared by the method described by Blaise (*Compt. rend.*, 1904, 138, 284). We have to thank Mr. E. J. Holmyard for the specimen of citral.

Solutions.

Acraldehyde.—The absorption curve of this substance in alcohol has been drawn (Fig. 1, I), from which it will be seen that there is one band the head of which is at about $1/\lambda$ 3150.

Crotonaldehyde.—The absorption curve (Fig. 1, II) shows one band at $1/\lambda$ 3130, which is weaker than that of acraldehyde.

Citral.—The absorption curve (Fig. 1, III) shows a very weak band at $1/\lambda$ 3030; and, on the more refrangible side, a still weaker one at $1/\lambda$ 4300, which, on the original photograph, appears more like a rapid extension of the rays between about λ 2500— λ 2280.

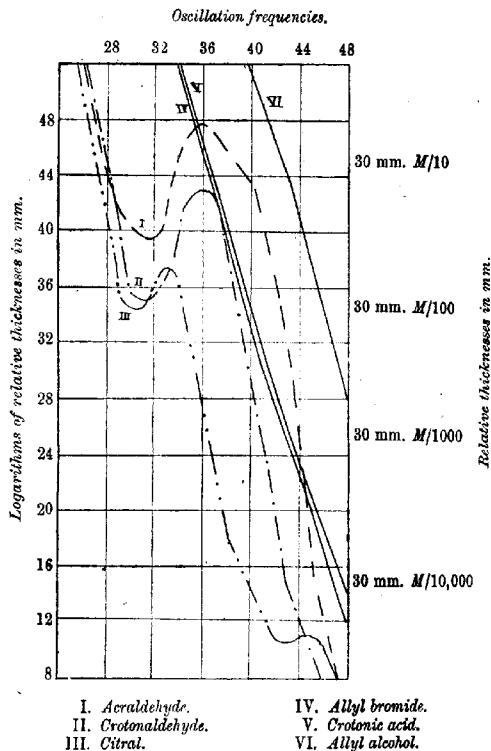
Allylacetone.—The absorption curve (Fig. 2, I) shows one band at $1/\lambda$ 3620.

Methyl Allyl Ketone.—The absorption curve of the substance in ether (Fig. 2, II) shows one band at $1/\lambda$ 3450.

Methyl Propenyl Ketone.—The absorption curve of the substance in ether (Fig. 2, III) shows one band at $1/\lambda$ 3100. The band is very similar to that of methyl allyl ketone, and differs mainly in the position.

Mesityl Oxide.—The curve (Fig. 2, IV) shows a very weak band at about $1/\lambda$ 3200, which is weaker than the corresponding band of methyl allyl ketone and a second very weak band at $1/\lambda$ 4200, which on the photograph is more like a rapid extension of the rays

FIG. 1.



between λ 2500— λ 2200, and it corresponds with the more refrangible band of phorone.

Phorone.—Baker and Baly (T., 1907, **91**, 1128) showed that the substance in solution had two bands, one at $1/\lambda$ 2850, and a stronger band at $1/\lambda$ 3730 in much weaker solutions. The authors have confirmed this observation.

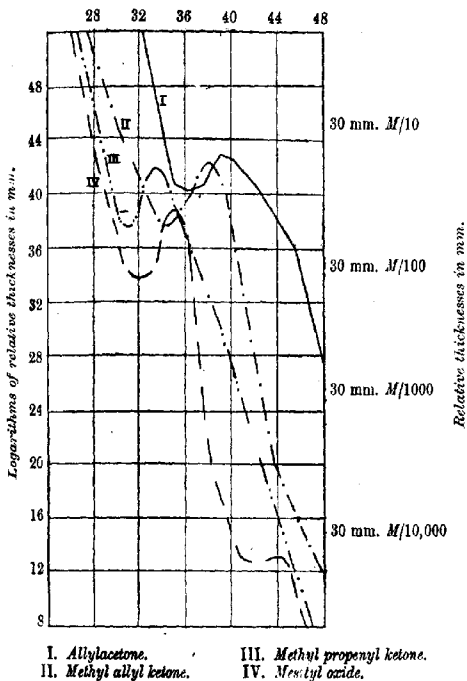
Allyl Alcohol.—Hartley (T., 1881, **39**, 153), Drossbach (Ber., 1902, **35**, 1486), and Magini (Nuovo Cim., 1903, [v], **6**, 343) have

shown that solutions of this substance had no bands. The authors have repeated the experiments, and have drawn the line of general absorption (Fig. 1, VI).

Allyl Bromide.—Ethereal solutions of this substance were also examined, but no bands were observed. The line of general absorption has been drawn (Fig. 1, IV).

FIG. 2.

Oscillation frequencies.



Crotonic Acid.—Solutions of this substance showed no band at any dilution. The line of general absorption has been drawn (Fig. 1, V). Stewart (T., 1907, 91, 203) had also obtained a similar result.

Results of the Examination of the Solutions.—The results of the investigation of the absorption of the solutions are that the aldehydes and the ketones alone show specific absorption bands,

the lighter substances having one band, and the heavier menthyl oxide, phorone, and citral showing two bands.

Vapours.

Acetaldehyde.—The absorption by the vapour of this substance may be described as a broad band, the less refrangible edge of which is broken up into a series of finer bands. The following table contains the measurements of the more refrangible edges of these narrow bands observed in the vapour, in a 200 mm. tube at 22° and 253 mm. pressure, using an acetylene light as the source of radiation. The vapour was also investigated at temperatures varying from 17° to 90°, and at increased pressures, the chief effect being that the weaker bands became stronger and more diffuse, and the general absorption was gradually extended towards the less refrangible regions. It is proposed to study these bands later with an instrument of greater dispersion than was available at the time.

TABLE A.

The Absorption Bands of Acetaldehyde Vapour in a 200 mm. Tube at 22° and 253 mm. Pressure.

Abbreviations: w.=weak; v.w.=very weak; mod.w.=moderately weak; str.=strong; f.str.=fairly strong; diff.=diffuse; narr.=narrow.

λ .	λ .	λ .
4080 v.w.	3775 str.	3610 v.w.
4040 w.	3765 w., narr.	3600 "
4025 w.	3755 v.w., narr.	3590—3585 mod. wide
4010 v.w.	3740 " "	3580 mod. w.
3975 v.w., diff.	3730 " "	3570 "
3930 " "	3710 w.	3565 "
3895 w.	3700 w., diff.	3560 "
3890 v.w., narr.	3695 w.	3555 w.
3870 v.w.	3685 mod. str. & wide	3550 w.
3850 str., mod. wide	3680—3660 mod. str.	3540 w.
3830 f.str. "	& wide	3535 w.
3820 w., narr.	3655—3650 mod. str.	3520 mod. w.
3810 " "	& wide	3515 v.w.
3800 " "	3640 mod. w.	3510—3490 w.
3790 " "	3630 "	3485—3475 v.w.
	3625 "	3465 v.w.
	3620 "	3460 "
	3618 "	3450 "
	3615 "	

At about λ 3440 a broad band begins; and, using the cadmium spark as the source of light, a photograph showed that it extended, at 22° and 750 mm., to about λ 3060, and was diffuse on the more refrangible edge. Beyond this, the rays were transmitted to about λ 2270, where general absorption began.

There are several groups of the bands which are quite comparable in their general appearance, and amongst those the two groups *A* and *A'* are unmistakable. Also, there are several series of doublets and triplets representing bands of very similar appearance.

Crotonaldehyde.—The absorption by the vapour of this substance may, like that of acetaldehyde, be described as a broad band, the less refrangible edge of which is broken up into a series of weak, narrow bands. The following table contains the measurements of the more refrangible edges of the finer bands observed in a 200 mm. tube at 16° and 751 mm. pressure, using an acetylene light as a source of radiation. The vapour was also examined at temperatures ranging from 16° to 90° and at increased pressures, the chief effect being that the weaker bands became stronger and more diffuse, and some of them widened into each other, whilst the general absorption extended more towards the less refrangible regions.

TABLE B.

The Absorption Bands of Crotonaldehyde Vapour in a 200 mm. Tube at 16° and 751 mm. Pressure.

Abbreviations: w.=weak; v.w.=very weak; mod.w.=moderately weak; mod.str.=moderately strong.

λ .	λ .
3955 w.	{ 3640 v.w.
3785 v. w.	{ 3635 "
3775 "	{ 3600 "
3760 mod. str.	{ 3590 "
{ 3730 v.w.	3570 mod. w.
{ 3720 "	3560 v.w.
3700 "	3550 "
3690 mod. w.	3540 "
{ 3675 v.w.	
{ 3670 "	

On the more refrangible side of λ 3540 there are also several very weak finer bands, but they are too faint to measure them with any degree of accuracy. The broad band on the more refrangible side of the narrow bands expands and covers over some of the finer bands at increased temperatures and pressures. The position of the broad band, using the copper spark as the source of light, may be described as follows:

$^{\circ}$.	Pressure in mm.	
60	851	The rays were absorbed between λ 3500— λ 3050 and then transmitted to λ 2470, when general absorption began.
75	881	The rays were absorbed between λ 3650— λ 2910 and then transmitted to λ 2510, when general absorption began.
90	911	The rays were absorbed between λ 3700— λ 2830 and then transmitted to λ 2600, when general absorption began.

438 PURVIS AND MCCLELAND: THE ABSORPTION SPECTRA OF

The bands are not so strong as those of acetaldehyde; they are fewer in number, and they appear to consist mainly of doublets.

Citral.—There was considerable difficulty in the study of the vapour of this substance in consequence of its high boiling point and the weakness of the bands. When several drops of the liquid were placed in the 200 mm. absorption tube, the following phenomena were observed:

ϵ .	Pressure in mm.	
12	753	The rays were transmitted to about λ 2230.
30	797	" " " λ 2270.
45	823	" " " λ 2400.
60	853	" " " λ 2480.
75	883	" " " λ 2550, and there were traces of a weakening between λ 3300— λ 3050.
90	913	The rays were transmitted to about λ 2650, and there was a more marked weakening between λ 3300— λ 3030.

That is to say, between 30° and 45° there was a rapid absorption of the rays on the more refrangible side between λ 2400— λ 2270, denoting a very weak band, and comparable with a very weak solution band on the more refrangible side, and also traces of a very weak band on the less refrangible side between λ 3300— λ 3030 and comparable with the corresponding solution band. There were no traces of a resolution into a series of finer bands.

Allylacetone.

ϵ .	Pressure in mm.	
15	759	The rays were transmitted to λ 2120.
30	803	" " " λ 2130.
45	829	" " " λ 2140.
60	859	" " " λ 2150; but they were weak between λ 2950— λ 2620.
75	889	The rays were transmitted to λ 2960; they were then absorbed to about λ 2530, and then transmitted to λ 2170.
90	919	The rays were absorbed between λ 3070— λ 2330, although the Cd lines 2748 and 2578 were feebly visible, and the series of Cd lines λ 2329 to λ 2265 were strong.

That is to say, the vapour of allylacetone has one band comparable with the solution band, and it is not resolved into a series of finer bands.

Methyl Allyl Ketone.

ϵ .	Pressure in mm.	
13	747	The rays were transmitted to about λ 2360.
30	781	" " " λ 2400, but they were weak between about λ 3000— λ 2750.
45	817	The rays were absorbed between λ 3050— λ 2700 and then transmitted to λ 2440.

Pressure in mm.		
60	847	The rays were absorbed between λ 3100— λ 2650 and then transmitted to λ 2430.
75	877	The rays were transmitted to λ 3260; the Cd line 2573 was just visible.
90	923	The rays were transmitted to λ 3400.

The observations show* that the vapour of methyl allyl ketone as one band comparable with the solution band, and that it is not resolved into a series of finer bands.

Methyl Propenyl Ketone.

Pressure in mm.		
12	741	The rays were transmitted to λ 2410.
30	785	" " " " λ 2470, but there was a little weakening between about λ 3300— λ 3060.
45	811	The rays were transmitted to λ 2590, but there was a definite weakening between about λ 3400— λ 3020.
60	841	The rays were absorbed between about λ 3500— λ 3000 and then transmitted to λ 2740.
75	871	The rays were transmitted to about λ 3570, but the Cd lines 3466, 2980, 2880, 2748 were just visible.
90	901	The rays were transmitted to 3620.

These observations show that the vapour of methyl propenyl ketone has one band comparable with the solution band, and that it is not resolved into finer bands.

Mesityl Oxide.

Pressure in mm.		
16	747	The rays were transmitted to λ 2510.
30	791	" " " " λ 2560.
45	817	" " " " λ 2610, but they were weak between λ 3450—3020.
60	847	The rays were absorbed between λ 3600— λ 2890 and then transmitted to λ 2640.
75	877	The rays were absorbed between λ 3650— λ 2820 and then transmitted to λ 2670.
90	907	The rays were absorbed between λ 3710— λ 2770 and then transmitted to λ 2690.

Experiments were conducted at 12° and 740 mm. pressure when the absorption tube contained a very small quantity of the vapour of mesityl oxide, in order to see if there were any traces of a more refrangible band comparable with that of the solution. It was noticed that the rays were transmitted to about λ 2370; there was weak absorption to about λ 2300, and then complete absorption beyond. This is comparable with the more refrangible solution band. So that there were two vapour bands, which were not resolved into finer bands. The continuous spectrum of an acetylene lamp

was also used to investigate the less refrangible band, but no fine bands were observed.

Phorone.

$^{\circ}\text{C.}$	Pressure in mm.	
15	745	The rays were transmitted to λ 2480; they became weak up to about λ 2250, and then feebly transmitted to λ 2180.
20	775	The rays were transmitted to λ 2550; they were absorbed to about λ 2330, and then feebly transmitted to about λ 2170.
30	789	The rays were transmitted to λ 2660.
45	815	" " " λ 2710.
60	845	" " " λ 2740.
75	875	" " " λ 2780, but they were weak between λ 3900— λ 3450.
90	905	The rays were transmitted to λ 4000; they were absorbed from λ 4000— λ 3350, and then transmitted to λ 2810.
100	921	The rays were absorbed between λ 4010— λ 3320, and then transmitted to λ 2850.

That is to say, there were two bands comparable with the solution bands; but there was no resolution of these bands into a series of fine bands, similar to those observed in acetaldehyde and crotonaldehyde. The continuous spectrum of an acetylene lamp was also used to investigate the less refrangible band, but no fine bands were observed.

Allyl Alcohol.

$^{\circ}\text{C.}$	Pressure in mm.	
30	808	The rays were transmitted to λ 2100.
45	834	" " " " λ 2200.
60	864	" " " " λ 2270.
75	894	" " " " λ 2500; the series of Cd lines λ 2329— λ 2265 were visible.
90	924	The rays were transmitted to λ 2630.

The light of an acetylene lamp was also used to investigate the less refrangible regions to about λ 2800, but no bands were observed.

Allyl Bromide.

$^{\circ}\text{C.}$	Pressure in mm.	
15	754	The rays were transmitted to λ 2590.
30	809	" " " " λ 2670.
45	834	" " " " λ 2720.
60	864	" " " " λ 2760.
75	894	" " " " λ 2850.
90	924	" " " " λ 3140.

That is to say, neither the vapours of allyl alcohol nor allyl bromide showed any trace of absorption bands. The whole of the bands found in acetaldehyde have completely disappeared.

Crotonic Acid.

f.	Pressure in mm.	
15	764	The rays were transmitted to λ 2130.
30	808	" " " " λ 2150.
45	834	" " " " λ 2190.
60	864	" " " " λ 2230.
75	894	" " " " λ 2270, the series of Cd lines λ 2320—2265 were very weak.
90	924	The rays were transmitted to λ 2570; the Cd lines λ 2821 and λ 2813 were just visible.

An acetylene lamp was also used for the less refrangible regions; but no band was observed. The experiments show that the vapour of crotonic acid has no band; the whole of the bands found in crotonaldehyde have completely disappeared.

Results of the Examination of the Vapours.—The results of the vapours are to show that only in acetaldehyde and crotonaldehyde are there a series of fine bands on the less refrangible edges of a large strong band. None of these narrow bands occurs in the other ketones and aldehydes, which are characterised by wide bands comparable with the solution bands. Further, the corresponding alcohol, halogen derivative, and acid show no specific absorption, results which were similar in the solutions of these substances.

Discussion of the Results.—The more important results of this investigation are: (1) the considerable number of narrow bands found in the vapours of acetaldehyde and crotonaldehyde, and which are absent from their solutions; (2) the absence of similar narrow bands from the vapours of other unsaturated aldehydes, ketones, alcohol, and acid; and the close similarity of their specific and general absorptions with those of the solutions.

If the absorption spectrum of acetaldehyde is compared with that of propionaldehyde (*loc. cit.*), it will be noticed that the difference lies in a considerable shift of the band towards the less refrangible part of the spectrum, accompanied by its resolution into a series of narrow bands in the vapours. It is suggested that this is caused by the introduction of the ethenoid linking into the aldehyde, and that the change produces an effect comparable with that observed by the introduction of a second carbonyl group; and, further, that although all the atoms in a molecule are concerned in the final result, the fundamental influence originates in these primary oscillation centres. The results of this change were described by the authors in the first paper of this series (*loc. cit.*), and differ from those described above in the position of the less refrangible band, and in the fact that the more refrangible diffuse band of glyoxal and of dimethyl diketone is not observed in the spectrum of

acraldehyde nor of crotonaldehyde, although it appears in the spectra of mesityl oxide, of citral, and of phorone.

Now the bands in glyoxal have been explained as the result of the interaction of two primary oscillation centres; and it was suggested that they are the consequence of electron vibrations governed by the laws expressed by the following equations*:

$$l \frac{d^2x}{dt^2} + m \frac{d^2y}{dt^2} + r \frac{dx}{dt} + cx = E \cos pt.$$

$$m \frac{d^2x}{dt^2} + l \frac{d^2y}{dt^2} + r \frac{dy}{dt} + cy = E \cos pt.$$

The authors propose to extend this explanation to the present case, on the assumption that an ethenoid linking also can function as a primary oscillation centre. A difficulty arises from the absence of direct observation of specific absorption in substances, such as ethylene, which have been found to be absolutely transparent within the limits available for ordinary observation in the ultraviolet. The possibility of selective absorption in the regions beyond $1/\lambda$ 5000 must not, however, be forgotten. The report of the Committee of the British Association (Portsmouth, 1911) on dynamic isomerism indicates the possibility of the head of a band at λ 1700 ($1/\lambda$ 5800) in allyl alcohol, a region which is far beyond the reach of a photographic plate. It is, therefore, not improbable that the absorption shown by these substances originates in the hypothetical band of the ethenoid linking, strengthened and widened by the influence of the substituent.

If, then, it be assumed that the double bond is a primary oscillation centre, equations can be applied differing from the above only in the inequality of the coefficients in the two equations, since the two centres of absorption are no longer similar. The deductions from the equations are (1) that in acraldehyde and similarly constituted substances there will be two bands, namely, one, originating in the carbonyl group, in the less refrangible regions of the spectrum; and the other, originating in the ethenoid linking, in the region of very short wave-lengths; and (2) that the less refrangible band will show a tendency to break up into a series of fine bands or lines. The second of the two bands is, in the lower members of the series, outside the region ordinarily examined; but it appears on weighting the molecule in the neighbourhood of the ethenoid double bond, as in mesityl oxide, citral, and phorone. In the latter substances there are two ethenoid linkings, but the interaction between them is likely to be negligible, even in the case of phorone, since they are not adjacent. They will, therefore,

* These equations were misprinted in the original paper.

merely reinforce one another in their action on the carbonyl group. This may explain the colour of phorone, where the band is displaced sufficiently into the visible spectrum for the colour to be noticed. In citral, however, the second double bond appears altogether too remote to produce any effect as regards colour, although the curving of the carbon chain might be thought to bring it into close proximity with the carbonyl group. In methyl allyl ketone and in allylacetone, where the two originating oscillation centres are separated by one and two methylene groups respectively, the phenomena observed are those indicated by the above hypothesis, the influence of the oscillation centres on one another falling off rapidly as their distance apart increases.

It will be noticed that, whereas the less refrangible bands of the vapours of acetaldehyde and crotonaldehyde readily resolve themselves into fine bands or lines (the former more readily than the latter), the higher members of the series do not show these phenomena. This effect has been noticed in other substances, as, for example, in the benzene series (Hartley, *Phil. Trans.*, 1908, A, 208, 475), the pyridine series (Purvis, T., 1910, 97, 692), and by the authors in the aldehydes (*loc. cit.*). It seems to bear the interpretation of a general statement, namely, that, in a homologous series, as the molecular weight increases, the narrow vapour bands tend to coalesce into a single broad band.

We venture to think that the theory may be applied to explain the colour of the quinones; for the internal vibrations of each of the carbonyl groups will be influenced by those of the two adjacent ethenoid linkings, and, in addition, by those of the other carbonyl group. Sufficient thrust is, therefore, developed on the band originating in this group so that colour is the result. When either the carbonyl groups are removed, as in quinol, or the double bonds saturated, as in cyclohexane-1:4-dione, the colour is destroyed, although there is still specific absorption in the ultraviolet. The colour of the fulgides may be explained on the same lines.

It will be noticed that this suggestion is very similar to Armstrong's theory in that colour is supposed to be caused by the presence of at least three unsaturated groups in the molecule. The authors, however, think that their suggestion covers more of the observed phenomena. It explains, for example, the colour of dimethyl diketone and kindred substances, and it is unaffected by the absence of colour in imino-*p*-benzoquinone.

It should be added that the great influence of the carbonyl group in the production of colour has previously been discussed by one of us (Purvis, T., 1910, 97, 2535; 1911, 99, 107), but at that time there was not sufficient material for a more extensive development

of the subject; and in the case of none of these substances was it possible to study the vapour.

The authors are continuing the investigations with unsaturated hydrocarbons and other substances, and they desire to thank the Government Grant Committee of the Royal Society, by whose assistance some portion of the cost of the research was defrayed.

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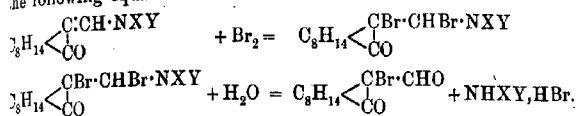
LII.—*A Novel Method for Resolving Externally Compensated Amines: Derivatives of d- and l-Oxymethylenecamphor.*

By WILLIAM JACKSON POPE and JOHN READ.

EXTERNALLY compensated amines are usually resolved into their optically active components by crystallisation with an optically active acid in the manner suggested and applied by Pasteur; although the applications of this method of resolution have been greatly extended by the use of the optically active camphorsulphonic acids, as introduced by Pope and Peachey (T., 1898, 73, 893), it quite frequently proves unavailing, owing either to the formation of partly racemic compounds or to unfavourable solubility relations between the two salts, *dAdB* and *dAlB*, produced. A method for resolving externally compensated primary amines, which embodied a new and useful idea, was devised by E. Erlenmeyer, jun. (Ber., 1903, 36, 976; *Annalen*, 1904, 337, 307); this consists in condensing the amine with the aldehyde *d*-helicin and separating the *d*-helicin derivatives formed from the *d*- and the *l*-base by fractional crystallisation. Although the base is readily recovered from the condensation products by an easy hydrolysis, it is not to be anticipated that the method will prove of very general applicability; since the condensation products are glucosides their crystallisation may be expected to give difficulty. As is well known, other methods similar in character have been employed, but none have hitherto found extensive application.

We have previously shown that the condensation products formed from *d*-oxymethylenecamphor and a primary or secondary externally compensated amine can be used for the purpose of ascertaining whether the amine used is externally compensated or potentially optically inactive (T., 1909, 95, 171); in the former case two con-

condensation products are obtained, one containing the residue of the *l*- and the other of the *d*-base, whilst if the amine is potentially optically inactive only one acidic amide results. More recently we have shown (T., 1912, 101, 2337) that the condensation product, $\frac{1}{8}\text{H}_{14}\text{C}(\text{CO})\text{CH}\cdot\text{NXY}$, is decomposed quantitatively, by titration in alcoholic solution with bromine, yielding bromo-oxymethylenecamphor and the hydrobromide of the amine, in accordance with the following equations:



These equations are very similar to those given by Aschan and Brühl (*Ber.*, 1894, 27, 2400) as representing the formation of bromo-oxymethylenecamphor and alkyl bromide by the action of bromine and water on the alkyl esters of oxymethylenecamphor.

d- and *l*-Oxymethylenecamphor.

These substances were prepared from *d*- and *l*-camphor by Bishop, Claisen, and Sinclair's method (*Annalen*, 1894, 281, 331); the previously unknown *l*-oxymethylenecamphor exhibits properties corresponding with those of its *d*-isomeride. The rotation constants and rotatory dispersions were determined with specimens which had been recrystallised from petroleum and left in a vacuum desiccator for two days; all the rotatory-power measurements given in the present paper were made, unless otherwise stated, on solutions prepared by making up the weight of material stated to 30 c.c. with the solvent, and examining the solution in a 4-dcm. tube at 20°.

Solvent: Ethyl Alcohol.

<i>d</i> -Oxymethylenecamphor.				<i>l</i> -Oxymethylenecamphor.			
0.3027 gram. Time, 30 minutes.				0.3023 gram. Time, 30 minutes.			
	H _g green.	H _g yellow.	N _{ay} yellow.		H _g green.	H _g yellow.	N _{ay} yellow.
α	+9.77°	+8.44°	+7.98°		-9.65°	-8.35°	-7.87°
$[\alpha]$	+242	+209	+198		-239	-207	-195
$[\text{M}]$	+436	+376	+356		-431	-373	-352
Rotatory dispersions: 1.224; 1.058.				1.226; 1.061.			
Time, 20 hours.				Time, 20 hours.			
α	+9.21°	+7.99°	+7.54°		-9.11°	-7.90°	-7.44°
$[\alpha]$	+228	+198	+187		-226	-196	-185
$[\text{M}]$	+411	+356	+336		-407	-353	-332
Rotatory dispersions: 1.221; 1.060.				1.224; 1.062.			
VOL. CIII.				G G			

The rotatory dispersions stated in this and the following determinations are, first, that for Hg_{green}/Na_{yellow} and secondly, that for Hg_{yellow}/Na_{yellow} . Although the compounds exhibit marked mutarotation and the extent and velocity of the mutarotation are known to be dependent on the quantity and nature of the impurity present, the above values agree well amongst themselves and with the values previously given for sodium light (T., 1909, 95, 176).

Externally compensated oxymethylenecamphor was prepared by allowing a solution of equal weights of the two components in light petroleum to crystallise slowly; it is indistinguishable in appearance and ordinary properties from the active isomerides, and melts at the same temperature, namely, 80–81°. Like the latter substances it becomes pasty and yellow with lapse of time.

d- and l-Bromo-oxymethylenecamphor.

Considerable quantities of the bromo-oxymethylenecamphors were obtained in the course of the present work, and, as no standard determinations of the rotation constants of these substances have been hitherto published, it is desirable to record the values. The following data refer to *d*-bromo-oxymethylenecamphor.

Solvent: Ethyl Alcohol.

	0.3564 gram. Time, 30 minutes.			0.3564 gram. Time, two days.		
	Hg_{green} .	Hg_{yellow} .	Na_{yellow} .	Hg_{green} .	Hg_{yellow} .	Na_{yellow} .
α	+4.07°	+3.68°	+3.48°	+3.94°	+3.58°	+3.40°
$[\alpha]$...	+85.7	+76.4	+73.2	+82.9	+74.3	+71.6
$[M]$...	+222	+198	+190	+215	+192	+185
Rotatory dispersions: 1.170; 1.043.				1.159; 1.038.		

Solvent: Ethyl Alcohol.

Solvent: Benzene.

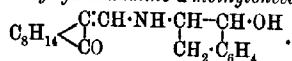
	1.0100 gram. Time, two days.			0.2549 gram. Time, 30 minutes.		
	Hg_{green} .	Hg_{yellow} .	Na_{yellow} .	Hg_{green} .	Hg_{yellow} .	Na_{yellow} .
α	+11.58°	+10.29°	+9.91°	+3.14°	+2.82°	+2.74°
$[\alpha]$...	+86.0	+76.4	+73.6	+92.4	+83.0	+80.6
$[M]$...	+223	+198	+191	+239	+215	+209
Rotatory dispersions: 1.189; 1.038.				1.146; 1.029.		

Although this substance shows little evidence of the occurrence of dynamic isomerism, behaving as if it had the true aldehydic constitution, it exhibits a slight but appreciable mutarotation in alcoholic solution; the rotation values become constant after two days. No mutarotation is to be observed in the benzene solutions.

l-Bromo-oxymethylenecamphor corresponds in properties with its enantiomorphously related isomeride.

Externally Compensated Bromo-oxymethylenecamphor.

On crystallising equal quantities of the two optically active isomerides from alcohol the externally compensated substance is obtained in large, well-developed, almost square plates; it is less soluble than its components, forms much larger crystals, and exhibits no tendency to separate as an oil, as do the components. It melts at 46.5° , whilst the *d*- or *l*-isomeride melts at 44° . Both the active and externally compensated substances crystallise in nearly square plates, which show extinctions bisecting the angles, and probably belong to the orthorhombic system. After melting on a microscope slide, the three substances solidify to plates exhibiting slight double refraction; the modification thus first formed soon changes to a form identical with that deposited from solution. The close similarity in behaviour between the active and inactive isomerides suggests that the latter is not a racemic compound, although this is indicated by its sparing solubility.

l-Hydroxyhydrindamino-d-methylenecamphor,

We have previously shown that externally compensated hydroxyhydrindamine can be very easily and completely resolved into its optically active components by crystallisation with *d*- and *l*-bromocamphor- π -sulphonic acid (T., 1912, 101, 758). As a preliminary to effecting the resolution of the base by means of *d*-oxymethylenecamphor, the condensation products of the latter with the optically active amines were prepared.

The calculated quantity of *d*-oxymethylenecamphor dissolved in alcohol is added to a solution of *l*-hydroxyhydrindamine dissolved in 50 per cent. acetic acid, and the mixture warmed for a short time on the water-bath; dilute sodium hydroxide solution is then added, and the precipitated oil, which soon becomes semi-crystalline, washed with water and dissolved in warm alcohol. Water is added to the alcoholic solution in quantity just insufficient to produce turbidity, and the solution allowed to remain; *l*-hydroxyhydrindamino-*d*-methylenecamphor is then slowly deposited in colourless, six-sided, striated plates, which, after recrystallisation from aqueous alcohol, melt at 122° . The crystals obtained are complex interpenetration twins of a uniaxial material, and are extremely soluble in most of the usual organic solvents, with the exception of light petroleum:.

0.0953 gave 0.2689 CO_2 and 0.0704 H_2O . C = 76.95; H = 8.27.

$\text{C}_{20}\text{H}_{25}\text{O}_2\text{N}$ requires C = 77.12; H = 8.10 per cent.

This substance exhibits very marked mutarotation in benzene, ethyl alcoholic, and glacial acetic acid solutions. A benzene solution containing 0.1552 gram in 30 c.c. gave the following values for α : after 52 minutes, $+0.58^\circ$; 92 minutes, $+1.09^\circ$; 152 minutes, $+1.76^\circ$; after 18 hours, $+2.73^\circ$, and became constant after 48 hours with $+2.71^\circ$ for the mercury-green line. An ethyl-alcoholic solution containing 0.1490 gram in 30 c.c. similarly gave the following values of α : after 30 minutes, $+3.10^\circ$; after 1 hour, $+3.13^\circ$; after 7 hours, $+3.34^\circ$; and a constant value of $+3.68^\circ$ after 72 hours. A glacial acetic acid solution containing 0.0974 gram in 30 c.c. gave the value of α $+2.01^\circ$ after 1 hour, and a constant value of $+1.66^\circ$ after 18 hours.

After the rotatory powers of the above three solutions had become constant they were carefully determined, with the following results; these values may be therefore taken as the constants for the material:

	Solution in benzene.			Solution in ethyl alcohol.		
	Hg _{green} .	Hg _{yellow} .	Na _{yellow} .	Hg _{green} .	Hg _{yellow} .	Na _{yellow} .
α	+2.71°	+2.21°	+2.05°	+3.68°	+3.12°	+2.89°
$[\alpha]$	+131	+107	+99.1	+185	+157	+145
$[M]$	+407	+333	+303	+575	+488	+451
Rotatory dispersions : 1.322 ; 1.078.				1.273 ; 1.080.		
	Solution in glacial acetic acid.					
	Hg _{green} .	Hg _{yellow} .	Na _{yellow} .			
α	+1.66°	+1.40°	+1.33°			
$[\alpha]$	+128	+108	+102			
$[M]$	+398	+336	+317			
Rotatory dispersions : 1.243 ; 1.053.						

Immediately after running bromine into an alcoholic solution of the substance until a faint, permanent yellow colour is obtained, the *hydrobromide* of the base separates in colourless, glistening needles; this salt is obtained in a pure condition by filtration and washing with acetone:

0.2440 required 10.6 c.c. $N/10\text{-AgNO}_3$. Br = 34.72.

$\text{C}_9\text{H}_{11}\text{ON}\cdot\text{HBr}$ requires Br = 34.74 per cent.

0.1556 gram, in 30 c.c. of aqueous solution, gave, for the mercury-green line, $\alpha -0.66^\circ$, whence $[\alpha] -31.8^\circ$ and $[M] -73.2^\circ$.

As the molecular rotatory power of *l*-hydroxyhydrindamine hydrochloride for mercury-green light in aqueous solution is $[M] -72.6^\circ$ (T., 1912, 101, 770), the hydrobromide now described is pure.

d-Hydroxyhydrindamino-*d*-methylenecamphor.

This substance is prepared in a similar manner to the isomeride described above; it crystallises readily from aqueous alcohol in

clusters of long, transparent needles, which soften at 115° , but only melt completely at 122° . It is the more soluble of the two isomerides:

0.1020 gave 0.2875 CO_2 and 0.0756 H_2O . $\text{C}=76.87$; $\text{H}=8.29$.

$\text{C}_{20}\text{H}_{25}\text{O}_2\text{N}$ requires $\text{C}=77.12$; $\text{H}=8.10$ per cent.

d-Hydroxyhydrindamino-d-methylenecamphor exhibits very marked mutarotation in benzene solutions: 0.1545 gram, made up to 30 c.c. with benzene, gave the following values of α for the mercury-green line: after 52 minutes, $+9.09^{\circ}$; after 82 minutes, $+9.00^{\circ}$; after 142 minutes, $+7.73^{\circ}$; after 24 hours, $+3.95^{\circ}$; after 54 hours the rotatory power became constant at $\alpha +3.92^{\circ}$. 0.1555 Gram, made up to 30 c.c. with ethyl alcohol, similarly gave the following values of α : after 30 minutes, $+9.83^{\circ}$; after 1 hour, $+9.78^{\circ}$; after 7 hours, $+9.23^{\circ}$; after 72 hours the rotatory power became constant with $\alpha +7.79^{\circ}$. The following determinations establish the rotation constants of the substances after equilibrium had become established in the two solutions just referred to:

	In benzene, 0.1545 gram.			In ethyl alcohol, 0.1555 gram.		
	Hg _{green} .	Hg _{yellow} .	Na _{yellow} .	Hg _{green} .	Hg _{yellow} .	Na _{yellow} .
α	$+3.92^{\circ}$	$+3.37^{\circ}$	$+3.16^{\circ}$	$+7.79^{\circ}$	$+6.61^{\circ}$	$+6.27^{\circ}$
$[\alpha]$	+190	+164	+153	+376	+325	+302
$[M]$	+592	+509	+477	+1169	+1042	+939
Rotatory dispersions:	1.241; 1.066.			1.242; 1.054.		

It is noteworthy that when the solutions of this substance in benzene and ethyl alcohol are examined immediately after being made up, the rotation constants are not greatly different in benzene and ethyl alcohol; the observed rotatory powers diminish rapidly in benzene solutions until, when constancy is attained, the specific rotatory powers for the several wave-lengths are just about one-half as great in benzene as in alcoholic solution. Both the condensation products described above are very stable in the presence of boiling concentrated hydrochloric acid or hot concentrated sodium hydroxide solution.

The *d-hydroxyhydrindamine hydrobromide* obtained by treating *d-hydroxyhydrindamino-d-methylenecamphor* with bromine and alcohol in the manner previously described was found to have the molecular rotatory power $[M] +73.0^{\circ}$ for the mercury-green line in dilute aqueous solution; it is thus evidently a pure substance.

Resolution of Externally Compensated Hydroxyhydrindamine.

Externally compensated hydroxyhydrindamine hydrochloride is dissolved in 50 per cent. acetic acid and warmed with one molecular proportion of *d-oxymethylenecamphor* in alcoholic solution, the

product being isolated as in the previously described cases. The aqueous alcoholic solution of the condensation product, when exposed in an open dish at the ordinary temperature, slowly deposits minute, glistening needles, melting at about 118° ; further crops of the same crystalline material are successively deposited, mixed with a little oily matter, which is caused to redissolve by the addition of alcohol.

The crude, crystalline deposit thus obtained proved to be practically pure *l*-hydroxyhydrindamino-*d*-methylenecamphor; 0.1436 gram, made up to 30 c.c. with benzene, gave a constant value for the mercury-green line of $\alpha + 2.54^{\circ}$ after 30 hours' keeping; whence $[\alpha] + 133^{\circ}$, the constant for the pure compound being $[\alpha] + 131^{\circ}$. On recrystallisation from aqueous alcohol the characteristic, composite, six-sided plates of the substance are obtained; 0.1608 gram, made up to 30 c.c. with ethyl alcohol, gave a constant value of $\alpha + 3.97^{\circ}$ for the mercury-green line after 50 hours' keeping; the specific rotatory power is thus $[\alpha] + 185^{\circ}$, a value identical with that for the pure substance stated above.

The separation of the *l*-component as its *d*-methylenecamphor derivative from the externally compensated amine can thus be effected very sharply indeed; as the isomeric *d*-hydroxyhydrindamino-*d*-methylenecamphor tends to separate as an oil, the isolation of the pure *d*-base is not conveniently attempted in the same operation. In accordance with previous experience it is, however, obviously possible to separate the latter isomeride with the aid of *l*-oxymethylenecamphor.

l-Hydroxyhydrindamine Hydrobromide.

This salt is conveniently obtained in a pure, crystalline condition, as previously indicated, by the action of bromine and alcohol on *l*-hydroxyhydrindamino-*d*-methylenecamphor; it forms long, colourless, glistening needles, and is very soluble in water:

0.2245 required 9.7 c.c. *N*/10-AgNO₃. Br = 34.53.

C₉H₁₁ON.HBr requires Br = 34.74 per cent.

The rotation constants of the salt in aqueous solution were determined for comparison with those of the hydrochloride (*loc. cit.* p. 770).

Solvent: water, 0.1507.			
	Hg _{green} .	Hg _{yellow} .	Na _{yellow} .
α	-0.64°	-0.55°	-0.53°
$[\alpha]$	-31.9	-27.4	-28.4
$[M]$	-73.3	-63.0	-60.7
$[M]$ for the pure hydrochloride.....	-72.6	-63.4	-61.1

Resolution of Externally Compensated α -Phenylethylamine.

In a previous paper we have referred to the difficulty of resolving externally compensated α -phenylethylamine (T., 1909, 95, 172), and have shown that on treatment with *d*-oxymethylenecamphor it yields two isomeric condensation products, which are very stable towards hydrolysing agents. The less soluble product melts at 145–148°, and was described in our previous paper as *d*- α -phenylethylamino-*d*-methylenecamphor; the results obtained from its decomposition now show it to be *l*- α -phenylethylamino-*d*-methylenecamphor. The more soluble condensation product melting at 112–114·5° is now proved to be somewhat impure *d*- α -phenylethylamino-*d*-methylenecamphor; the corrected names will be applied to the substances in the following pages.

l- α -Phenylethylamino-*d*-oxymethylenecamphor is readily separated in a pure state and in good yield from the product of treating the externally compensated amine with *d*-oxymethylenecamphor; its alcoholic solution readily decolorises bromine, but the hydrobromide of the base is not easily separated in a crystalline condition. The mixture of hydrobromide and *d*-bromo-oxymethylenecamphor obtained by the action of alcohol and bromine was therefore mixed with warm water and extracted with benzene; the aqueous solution of the hydrobromide was then treated with benzoyl chloride and sodium hydroxide, and benzoyl-*l*- α -phenylethylamine obtained. This substance separates from aqueous alcohol in fine, lustrous needles, melting at 119·5°, a lower value than that of 125·5° given by Marckwald and Meth (Ber., 1905, 38, 801); in a benzene solution containing 3·005 per cent. of the benzoyl derivative the latter workers obtained the specific rotatory power $[\alpha]_D -39·9^\circ$, whilst for the same concentration at 20° we obtained the nearly identical value of $[\alpha]_D -40·1^\circ$. This concentration represents a practically saturated solution. Marckwald and Meth showed that the specific rotatory power of this compound varies in a remarkable manner with the solvent, and we now find that the values in benzene solutions change considerably with the concentration; the following three sets of determinations refer to benzene solutions at 20°. Set I was made in 2-dm. tubes on a solution containing 0·6008 gram in 20 c.c., the concentration being thus 3·004 per cent.; solutions II and III were examined in 4-dm. tubes, and contained respectively 0·7152 gram and 0·2384 gram in 30 c.c., the concentrations being thus 2·3840 and 0·7947 per cent.

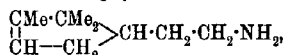
	I.			II.		
	Hg _{green} .	Hg _{yellow} .	Na _{yellow} .	Hg _{green} .	Hg _{yellow} .	Na _{yellow} .
α	-2·90°	-2·52°	-2·41°	-5·02°	-4·36°	-4·17°
$[\alpha]$	-48·3	-41·9	-40·1	-52·6	-45·7	-43·7
$[\eta]$	-137	-119	-114	-149	-129	-124
Rotatory dispersions: 1·203; 1·046.				1·204; 1·046.		

III.			
	Hg _{green} .	Hg _{yellow} .	Na _{yellow} .
α	-2.04°	-1.77°	-1.67°
$[\alpha]$	-64.2	-55.7	-52.5
$[M]$	-182	-158	-149
Rotatory dispersions: 1.222; 1.066.			

The *d*- α -phenylethylamino-*d*-methylenecamphor melting at 112—114.5° after subjection to a series of operations similar to that described in connexion with its isomeride, yielded a benzoyl derivative, which separated from aqueous alcohol in soft, opaque, feathery needles, melting at 110—111°; a 2.7 per cent. benzene solution of the benzoyl derivative gave $[\alpha]_D + 26.0^\circ$. By comparison with the data given above for the benzoyl derivative of the pure *l*-base it is seen that it contains only 80 to 85 per cent. of benzoyl-*d*- α -phenylethylamine. The method of resolving the externally compensated base now described is thus a very convenient one for the isolation of *l*- α -phenylethylamine and its derivatives, but cannot be economically applied to the preparation of the enantiomorphously related component; this latter could naturally be obtained by the use of *l*-oxymethylenecamphor.

Condensation of Oxymethylenecamphor with d- α -Camphylamine.

The primary base, α -camphylamine,



obtained by the reduction of α -campholenonitrile, has been but little studied; as it exhibits only a small rotatory power of $\alpha_D + 6^\circ$ in a 1-dm. tube (Tiemann, *Ber.*, 1896, **29**, 3009) it might be expected to consist of a mixture of two enantiomorphously related isomerides. Our method of ascertaining whether an amine is potentially inactive or resolvable into stereoisomerides, with the aid of *d*-oxymethylenecamphor, can be conveniently applied to this base, and we have therefore examined its condensation products.

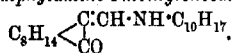
Our preparation of *d*- α -camphylamine boiled at 202—204° under one atmosphere pressure, instead of at 194—196° as stated by Tiemann; its density was $d = 0.8688$ at 20°, and it gave the following results on examination in a 4-dm. tube at 20°:

	Hg _{green} .	Hg _{yellow} .	Na _{yellow} .
α	+14.62°	+13.61°	+13.30°
$[\alpha]$	+4.27	+3.92	+3.83
$[M]$	+6.53	+6.00	+5.86
Rotatory dispersions: 1.099; 1.023.			

The rotatory power is thus smaller than that observed by

Fiemann, and it is further noteworthy that the rotatory dispersion for Hg_{green}/Na_{yellow} has an unusually low value.

d- α -Camphylamino-1-methylenecamphor,



On mixing an alcoholic solution of 1-oxymethylenecamphor with a solution of the base in dilute acetic acid the condensation product is immediately precipitated as an oil. After heating the mixture on the water-bath with the addition of sufficient alcohol to dissolve the oil, and allowing to cool slowly, a crystalline product separates; after collection and recrystallisation from warm acetone the compound is obtained in glistening, colourless needles, melting rather indefinitely at about 140° . On slow crystallisation from acetone it separates in long, well-developed, transparent prisms, which exhibit a fibrous cleavage, and slowly turn pink on exposure to the air:

0.1038 gave 0.3032 CO_2 and 0.0965 H_2O . $C = 79.66$; $H = 10.40$.

$C_{21}H_{33}ON$ requires $C = 79.93$; $H = 10.55$ per cent.

Since α -camphylamine is a primary amine it would be expected, in accordance with our previous results, that its *d*-methylenecamphor derivative would exhibit mutarotation in neutral solutions; the rotatory power of the alcoholic solutions does, indeed, change with lapse of time, although very slowly.

Solvent: Ethyl Alcohol.

	0.1065 gram. Time, 1 hour.			0.5028 gram. Time, 1 hour.		
	Hg_{green} .	Hg_{yellow} .	Na_{yellow} .	Hg_{green} .	Hg_{yellow} .	Na_{yellow} .
α	-4.17°	-3.54°	-3.33°	-19.69°	-16.69°	-15.76°
$[\alpha]$	-294	-249	-235	-294	-249	-235
$[\eta]$	-925	-785	-739	-925	-784	-741
Rotatory dispersions: 1.252; 1.063.				1.249; 1.059.		

The more dilute solution gave the following values of α for the mercury-green line: after 24 hours, -4.01° ; after 72 hours, -3.91° ; after 96 hours, -3.89° . The mutarotation, although slight, is therefore quite appreciable.

d- α -Camphylamino-*d*-methylenecamphor.

This substance is obtained in the same way as the foregoing, but in the preparation great care must be taken to free the crude product from traces of the original amine and oxymethylenecamphor, because otherwise crystallisation cannot be induced. The crude product is therefore extracted with light petroleum, and the solution shaken several times with dilute sodium hydroxide, and

subsequently with dilute hydrochloric acid; this treatment is repeated until crystalline material separates from the petroleum solution. The solid deposit is crystallised from warm acetone, and is then obtained in fine, glistening needles, melting at 155–158°. The pure compound is moderately soluble in warm acetone, but practically insoluble in light petroleum:

0.1045 gave 0.3066 CO₂ and 0.0970 H₂O. C=80.02; H=10.39.

C₂₁H₃₃ON requires C=79.93; H=10.55 per cent.

The following determinations of rotatory power were made with an alcoholic solution containing 0.1000 gram in 30 c.c. one hour after solution:

	Hg ^{green} .	Hg ^{yellow} .	Na ^{yellow} .
α	+3.31°	+2.73°	+2.65°
[α]	+248	+209	+197
[M]	+782	+637	+621

Rotatory dispersions: 1.259; 1.057.

The observed rotatory power, α , for mercury-green light changed in the following manner with lapse of time: after 26 hours, +2.33°; after 42 hours, +2.02°; after 67 hours, +1.76°. The mutarotation is thus more rapid than in the case of the previously described isomeride; it is noteworthy that the rotatory dispersions of the two substances are nearly the same.

As in the preparation of these two stereoisomerides no evidence was obtained of the formation of other products, it seems justifiable to conclude that the original base is an optically pure substance, and that it may be described as *d*- α -camphylamine.

Condensation of d- α -Camphylamine with dl-Oxymethylenecamphor.

The condensation of *d*- α -camphylamine with externally compensated oxymethylenecamphor occurs readily, and the product is caused to crystallise as described above. The resulting substance is, as is to be expected, a mixture of two stereoisomerides, but, owing apparently to the similar solubility of the isomerides and to the occurrence of tautomeric change, it was found impossible to effect a complete separation by fractional crystallisation. The specific rotatory power of the various fractions obtained varied between -66.4° and +5.0° in alcoholic solution for mercury-green light; no evidence was forthcoming in favour of the existence of a partly racemic compound which would have the specific rotatory power of [α] -23° for mercury-green light in alcoholic solution.

Separation of d-Bornylamine and d-neoBornylamine.

Considerable difficulties are frequently encountered in the attempt to separate the *cis*- and *trans*-isomerides of amines which

contain several asymmetric carbon atoms in the molecule; in view of the ease with which the resolution of externally compensated amines can be effected by the aid of the oxymethylenecamphors, it appeared desirable to apply the method to some instance of the kind just mentioned. One of the most difficult separations of this nature seems to be presented by the reduction product of *d*-camphoroxime described by Forster (T., 1898, **73**, 391; 1900, **77**, 1152), and shown by him to consist of a mixture of the *cis*- and *trans*-isomerides distinguished as *d*-bornylamine and *d*-neobornylamine; this mixture cannot be resolved by crystallisation with *d*- α -bromocamphor- π -sulphonic acid (Pope and Read, T., 1910, **97**, 987). Although the isolation of pure *d*-bornylamine from the mixture can be effected (compare Frankland, T., 1909, **95**, 2017) by fractionally crystallising the mixture of hydrochlorides, it presents considerable difficulties. Dr. Forster was so good as to provide us with several of his preparations, which represented mixtures of the hydrochlorides of *d*-bornylamine and *d*-neobornylamine in different proportion, for use in the present work; the experimental study of the condensation products which these materials yield with the oxymethylenecamphors has enabled us to devise a comparatively simple method for the preparation of pure *d*-bornylamine.

Preparation of Pure d-Bornylamine and its Derivatives.

A mixture of the hydrochlorides of the two isomeric bases, obtained during the working up of the reduction product of *d*-camphoroxime, was found to give the specific rotatory power for the mercury-green line in dilute aqueous solution of $[\alpha] + 9.4^\circ$; the molecular rotatory power is thus $[M] + 17.8^\circ$, corresponding with a content of about 79 per cent. of *d*-bornylamine hydrochloride. The solution of this mixture in 50 per cent. acetic acid was treated with the corresponding quantity of *d*-oxymethylenecamphor in ethyl-alcoholic solution in the manner already described; on warming for a short time on the water-bath a crystalline product separates, and, after addition of dilute sodium hydroxide solution, this is collected and washed with dilute hydrochloric acid and water. In one experiment 0.1038 gram of the product, made up to 30 c.c. with ethyl alcohol, and examined at 20° , gave the specific rotatory power $[\alpha] + 329^\circ$ after 4 hours, rising after 48 hours to $+ 345^\circ$, for the mercury-green line.

On allowing the concentrated solution in hot acetone of this crude product to remain, successive deposits of long, lustrous needles were obtained; the first five of these gave, for the mercury-green line, the specific rotatory powers, $[\alpha] + 387^\circ$, $+ 381^\circ$, $+ 368^\circ$, $+ 364^\circ$,

and +287° half an hour after being made up in alcoholic solution. Most of the crystalline material was contained in the first two fractions, and the mother liquor remaining after the deposition of the fifth fraction contained an extremely soluble substance. As the result of a considerable amount of experimental work it was ascertained that the first fraction consisted of pure *d*-bornylamino-*d*-methylenecamphor, and that the remaining crystalline fractions yielded this substance in a pure state after one recrystallisation from aqueous alcohol. The specific rotatory power varies from $[\alpha] +390^\circ$ to $+450^\circ$ for the mercury-green line in a freshly prepared 0.5 per cent. alcoholic solution, the precise value doubtless depending on the conditions attending crystallisation. The carefully purified substance forms long, colourless needles melting at 230°, and is moderately soluble in hot alcohol, but almost insoluble in acetone:

0.1151 gave 0.3368 CO₂ and 0.1105 H₂O. C=79.80; H=10.74.

C₂₁H₃₃ON requires C=79.93; H=10.55 per cent.

An ethyl-alcoholic solution containing 0.1058 gram in 30 c.c., examined in a 4-dcm. tube at 20°, gave the specific rotatory power $[\alpha] +396^\circ$ for the mercury-green line 30 minutes after having been made up; this value increased to $+410^\circ$ after 48 hours keeping, and was then constant. The standard determinations obtained after this interval are as follows:

After 48 hours. Solvent: Ethyl Alcohol. 0.1058 Gram.

	Hg _{green} .	Hg _{yellow} .	Na _{yellow} .
α	+5.79°	+4.90°	+4.65°
$[\alpha]$	+410	+347	+330
$[M]$	+1292	+1093	+1039

Rotatory dispersions: 1.245; 1.054.

The warm alcoholic solution of this substance reacts immediately with bromine, and, after evaporating off the alcohol on the water-bath, the residue is freed from *d*-bromo-oxymethylenecamphor by extraction of its aqueous solution with benzene; the aqueous residue is evaporated to dryness, and the crude hydrobromide purified by recrystallisation from acetone or by precipitation from its alcoholic solution by the addition of ether.

d-Bornylamine Hydrobromide.

In the process just above described this salt is obtained in thin, transparent, colourless prisms, which are extremely soluble in water or alcohol, and readily soluble in acetone; the yield is theoretical:

0.2016 required 8.6 c.c. N/10. AgNO₃. Br=34.09.

C₁₀H₁₉N.HBr requires Br=34.14 per cent.

Since this compound is a pure salt of *d*-bornylamine it appeared desirable to make the following standard determinations of its rotation constants.

Solvent: Water.

0.7396 gram in 30 c.c.				0.3070 gram in 30 c.c.			
	H _g green.	H _g yellow.	Na _g yellow.		H _g green.	H _g yellow.	Na _g yellow.
α	+2.04°	+1.82°	+1.74°		+0.85°	+0.76°	+0.72°
[α]	+20.7	+18.5	+17.6		+20.8	+18.6	+17.6
[M]	+48.4	+43.2	+41.3		+48.6	+43.5	+41.3
Rotatory dispersions: 1.172; 1.046.				1.181; 1.056.			

Solvent: Ethyl Alcohol.

1.4792 gram in 30 c.c.				0.4931 gram in 30 c.c.			
	H _g green.	H _g yellow.	Na _g yellow.		H _g green.	H _g yellow.	Na _g yellow.
α	+4.40°	+3.90°	+3.73°		+1.44°	+1.28°	+1.22°
[α]	+22.3	+19.8	+18.9		+21.9	+19.5	+18.6
[M]	+52.2	+46.3	+44.2		+51.2	+45.6	+43.4
Rotatory dispersions: 1.180; 1.046.				1.180; 1.048.			

Solvent: Chloroform.

0.2018 gram in 30 c.c.			
	H _g green.	H _g yellow.	Na _g yellow.
α	+0.86°	+0.72°	+0.70.
[α]	+32.0	+26.8	+26.0
[M]	+74.8	+62.6	+60.9
Rotatory dispersions: 1.229; 1.029.			

It is noteworthy that the rotation constants and the rotatory dispersions are nearly the same in aqueous and in alcoholic solution; it will be seen below that the same is true of solutions of *d*-neobornylamine hydrobromide.

Benzoyl-d-bornylamine.

This compound is prepared from the hydrobromide by the Schotten-Baumann reaction; it separates from aqueous alcohol in long, glistening needles, melting at 138.5°. Its rotatory-power determinations in ethyl-alcoholic solution yielded the following results:

1.2080 gram in 30 c.c.				0.3016 gram in 30 c.c.			
	H _g green.	H _g yellow.	Na _g yellow.		H _g green.	H _g yellow.	Na _g yellow.
α	-4.23°	-3.66°	-3.48°		-1.03°	-0.89°	-0.83°
[α]	-26.3	-22.7	-21.6		-25.6	-22.1	-20.6
[M]	-67.5	-68.4	-55.5		-65.8	-56.9	-53.0
Rotatory dispersions: 1.216; 1.052.				1.241; 1.072.			

Forster (*loc. cit.*) gives the melting point of this substance as 139° and the specific rotation as [α]_D -21.8° in alcoholic solution;

it is thus evident that his preparation was identical with ours. Similar values for the rotatory power were obtained by Frankland and Barrow (T., 1909, **95**, 2035).

It is therefore apparent that condensation with *d*-oxymethylenecamphor provides an easy method for separating pure *d*-bornylamine.

Separation of d-neoBornylamine and its Derivatives.

Reference has been made above to the presence of an extremely soluble material in the mother liquors, from which the *d*-bornylamino-*d*-methylenecamphor had been separated; this material represents the crude *d*-neobornylamino-*d*-methylenecamphor. In order to separate the latter substance in quantity use was made of a sample of the mixed hydrochlorides of the two amines which had the molecular rotatory power $[M] - 38.7^\circ$ for the mercury-green line in dilute aqueous solution, and hence contained about 61 per cent. of *d*-neobornylamine hydrochloride. This mixture of hydrochlorides was caused to condense with *d*-oxymethylenecamphor in the manner already described, and the condensation product fractionally crystallised first from light petroleum and then from acetone; a quantity of crystalline product, consisting of the small, glistening needles characteristic of *d*-bornylamino-*d*-methylenecamphor, was thus obtained. These fractions are almost insoluble in acetone, and readily yielded the pure *d*-bornylamine derivative when crystallised from alcohol or aqueous alcohol.

After separating as large a quantity as is possible of the *d*-bornylamino-*d*-methylenecamphor from the light petroleum solution, the very soluble material remaining in the mother liquors is recovered by evaporation, and fractionally crystallised from dilute alcohol. In this operation it is important to adjust the concentration of the solution and the proportion of water and alcohol present, so that crystallisation occurs slowly at a temperature just above the ordinary one; a series of levorotatory fractions is then obtained. In one particular operation five consecutive fractions separated, which had the specific rotatory powers $[\alpha] - 81.0^\circ$, -6.5° , -102.6° , 90.7° , and -76.9° for the mercury-green line in 0.5 per cent. alcoholic solutions at 20° ; the third of these proved to be nearly pure *d*-neobornylamino-*d*-oxymethylenecamphor, and the second contained nearly all of the *d*-bornylamine derivative which had resisted separation during the acetone crystallisation. The four fractions which gave the specific rotatory powers $[\alpha] - 81.0^\circ$, -102.6° , -90.7° , and -76.9° are more nearly identical than is indicated by these values, because the latter are disturbed by the mutarotation. On conversion into the hydrobromide of the base

by bromine and alcohol, as previously described, the salts obtained gave the specific rotations $[\alpha] -36.1^\circ$, -37.0° , -36.5° , and -34.3° respectively in dilute aqueous solution for the mercury-green line.

d-neoBornylamino-d-methylenecamphor.

This compound is obtained in a state of comparative purity by crystallising the highly laevorotatory fractions of the *d*-oxymethylenecamphor condensation product from aqueous alcohol until the rotatory power remains unchanged; it forms characteristic, striated scales, melting at 212° , and retaining a pale yellow colour which cannot be removed by recrystallisation. It is extremely soluble in alcohol, acetone, or light petroleum, and can only be conveniently crystallised from dilute alcohol:

0.1110 gave 0.3234 CO_2 and 0.1020 H_2O . $\text{C}=79.46$; $\text{H}=10.28$.

$\text{C}_{21}\text{H}_{33}\text{ON}$ requires $\text{C}=79.93$; $\text{H}=10.55$ per cent.

The rotation constants were determined in ethyl-alcoholic solution containing 0.1009 gram in 30 c.c., with the following results:

	After 1 hour.			After 48 hours.		
	H_{green}	H_{yellow}	N_{yellow}	H_{green}	H_{yellow}	N_{yellow}
α	-1.38°	-1.17°	-1.11°	-1.30°	-1.10°	-1.05°
$[\alpha]$	-103	-87.0	-82.5	-96.6	-81.8	-78.0
$[\text{M}]$	-923	-274	-260	-304	-258	-246
Rotatory dispersions: 1.243; 1.054.				1.238; 1.048.		

Both this compound and its isomeride strongly resist the action of the ordinary hydrolysing agents.

d-neoBornylamine Hydrobromide.

This salt is prepared from the foregoing substance by treatment with bromine and alcohol in the usual manner; it separates in hard, glistening, colourless crystals when its acetone solution is concentrated on the water-bath, and may be precipitated from alcoholic solutions in minute crystals by the addition of ether. It is very soluble in water, alcohol, or chloroform, and only moderately so in acetone; it is scarcely more soluble in the latter solvent when at than in the cold:

0.2622 required 11.1 c.c. $\text{N}/10\text{-AgNO}_3$. $\text{Br}=33.83$.

$\text{C}_{10}\text{H}_{19}\text{N}\cdot\text{HBr}$ requires $\text{Br}=34.14$ per cent.

The following determinations of rotatory powers were made:

Solvent: Water.

0.7410 gram.				0.3004 gram.			
	Hg ^{green} .	Hg ^{yellow} .	N ^{yellow} .	Hg ^{green} .	Hg ^{yellow} .	N ^{yellow} .	
α	-3.66°	-3.21°	-3.10°	-1.48°	-1.31°	-1.25°	
$[\alpha]$	-37.0	-32.5	-31.4	-37.0	-32.7	-31.2	
$[M]$	-86.6	-76.1	-73.5	-86.6	-76.5	-73.0	
Rotatory dispersions: 1.181; 1.035.				1.184; 1.048.			

Solvent: Ethyl Alcohol.

0.4910 gram.			
α	-2.58°	-2.26°	-2.18°
$[\alpha]$	-39.4	-34.5	-33.0
$[M]$	-92.1	-80.7	-77.2
Rotatory dispersions: 1.194; 1.046.			

Solvent: Chloroform.

0.2012 gram.		
-1.19°	-1.07°	-1.00°
-44.4	-39.9	-37.3
-104	-93.4	-87.3
1.190; 1.070.		

d-neobornylamine.

The aqueous solution of the above hydrobromide is treated with sodium hydroxide and extracted with light petroleum; after evaporating off the solvent and leaving for some time in a vacuum, any remaining traces of petroleum are removed by heating for a few minutes at 100°. The substance thus obtained exhibited the properties stated by Forster, and melted at 181°; the rotation constants were determined in alcoholic solution, 1.3239 grams being contained in 30 c.c.

	Hg ^{green} .	Hg ^{yellow} .	N ^{yellow} .
α	-7.84°	-6.97°	-6.70°
$[\alpha]$	-44.4	-39.5	-38.0
$[M]$...	-67.9	-60.4	-58.1

Rotatory dispersions: 1.170; 1.040.

The purest sample of *d-neobornylamine* obtained by Forster gave the value $[\alpha]_D -43.7^\circ$ in a 4 per cent. alcoholic solution; the base which we obtained gave $[\alpha]_D -38.0^\circ$ under the same conditions. Forster's determination was probably made with pure *d-neobornylamine*, and, if so, our product contained about 94 per cent. of this substance; thus, in spite of the extreme solubility of *d-neobornylamino-d-methylenecamphor*, an approximate separation of the isomeric bases can be achieved by the method now given. With the comparatively small amount of material in our possession it was not practicable to attempt further purification, but it is clear that considerable difficulty would attend the isolation of pure *d-neobornylamine* by our method alone. It is, however, important to notice that the approximate separation we have effected does not depend on the composition of the initial mixture of the two bases (compare Forster, T., 1900, 77, 1158), and it may thus be anticipated that a convenient mode of isolating pure *d-neobornyl-*

amine would result from combining the two methods, using our method for the preliminary separation, and that of Forster for the final purification. It also appears that the approximately pure *l-neobornylamine* hydrobromide can be further purified simply by repeated crystallisation from acetone.

The values for the rotation constants of the *d-neobornylamine* derivatives given do not, of course, refer to pure materials, but they may be advantageously quoted in view of the paucity of data available for this interesting base. The benzoyl derivative prepared from our specimen melted at 112–115°, and gave the values $[\alpha] -60.2^\circ$, -52.1° , and -50.0° for the mercury-green, mercury-yellow, and sodium-yellow rays respectively in a 1.8 per cent. alcoholic solution; Forster gives $[\alpha]_D -44.7^\circ$ under these conditions.

Condensation of l-Oxymethylenecamphor with the Bornylamines.

It was hoped that on condensing the mixture of *d-bornylamine* and *d-neobornylamine* with *l-oxymethylenecamphor*, the order of solubility of the two products might be the reverse of that observed when *d-oxymethylenecamphor* is used. *d-neoBornylamino-l-methylenecamphor* proved, however, to be more soluble than *bornylamino-l-methylenecamphor*, and both were found to be more soluble than the isomerides containing the *d-methylenecamphor* residue; a long series of fractional crystallisations showed that no advantage was to be gained by the application of *l-oxymethylenecamphor* to the separation.

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LIII.—*The Mode of Combustion of Carbon.*

By THOMAS FRED ERIC RHEAD and RICHARD VERNON WHEELER.

In previous papers ("The Rate of Reduction of Carbon Dioxide by carbon," T., 1912, 101, 831; "The Combustion of Carbon," T., 1912, 101, 846) we have shown that a consideration of the relative rates of the various reactions between oxygen, carbon monoxide, carbon dioxide, and carbon leads to the conclusion that, in the burning of carbon, the two oxides are produced simultaneously. That is to say, neither is the "primary" product of oxidation of carbon in the sense that it takes precedence over the other. It was

left to a succeeding paper to explain the manner in which this simultaneous production of the two oxides takes place.

In the present paper we describe experiments designed to solve this problem, and, on the strength of these experiments, we put forward an hypothesis as to the manner in which solid carbon burns, which appears to us to leave no known fact unexplained.

The experiments show that carbon, at all temperatures up to 900° and probably above that temperature, has the power of pertinaciously retaining oxygen. This oxygen cannot be removed by exhaustion alone, but only by increasing the temperature of the carbon during exhaustion. When quickly released in this manner it appears, not as oxygen, but as carbon dioxide and carbon monoxide. The proportions in which it appears in these two oxides when completely removed depend on the temperature at which the carbon has been heated during oxygen-fixation.

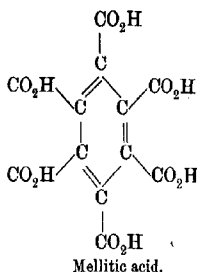
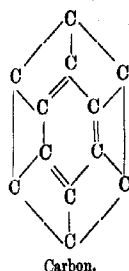
No physical explanation alone can account for this "fixation" of oxygen, but, in all probability, it is the outcome of a physico-chemical attraction between oxygen and carbon. Physical, inasmuch as it seems hardly possible to assign any definite molecular formula to the complex formed, which, indeed, shows progressive variation in composition; chemical, in that no isolation of the complex can be effected by physical means.

Decomposition of the complex by heat produces carbon dioxide and carbon monoxide. At a given temperature of decomposition these oxides make their appearance in a given ratio. Further, when a rapid stream of air at a given temperature is passed over carbon (which has previously been "saturated" with oxygen at that temperature), carbon dioxide and carbon monoxide appear in the products of combustion in nearly the same ratio as they do in the products of decomposition of the complex at that temperature.

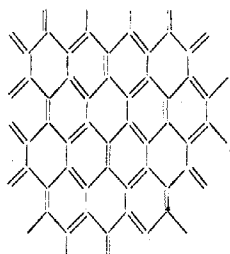
Our hypothesis is that the first product of combustion of carbon is a loosely formed physico-chemical complex, which can be regarded as an unstable compound of carbon and oxygen of an at present unknown formula, C_xO_y . It is probable that no definite formula can be assigned to this complex.

Our conception of what takes place during the combustion of carbon is, briefly, as follows: each oxygen molecule that comes into collision with the carbon becomes "fixed," in so far as it is rendered incapable of further progress by the attraction of several carbon molecules. We have as yet no absolute knowledge of the number of atoms contained in the carbon molecule. The formation of benzenhexacarboxylic acid (mellitic acid) by the oxidation of either amorphous carbon or graphite, warrants the assumption that

the carbon molecule contains not less than twelve atoms, possibly arranged in the following manner (Dewar, *Chem. News*, 1908, **97**, 16):



According to Aschan (*Chem. Zeit.*, 1909, **33**, 561), this representation of the molecule of carbon as two concentric benzene nuclei does not harmonise with the strain theory; for whilst carbon is an exceedingly stable substance, the strain in such a molecule must be greater even than that in a molecule of an explosive substance such as acetylene. On several grounds, which are discussed at length in the original paper, Aschan suggests an unstrained arrangement of benzene nuclei of the following type:



It may be, therefore, that in the oxidation of carbon the oxygen molecule actually enters the carbon molecule, a rearrangement of atoms taking place. However, for the present it is sufficient to assume that several carbon molecules hold one oxygen molecule, in bond as it were, and do not allow it to escape in conjunction with one of their atoms. A considerable evolution of heat takes place during this attachment of oxygen molecules, so much so that some of them eventually acquire sufficient energy to seize hold of a carbon atom and depart with it as carbon dioxide. Some of them become torn apart in the process—become atomised—and leave the carbon molecule as carbon monoxide.

This formation of a complex, and partial decomposition as fresh

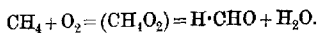
oxygen molecules become attached, goes on until the carbon becomes "saturated," the products of combustion during this period (a comparatively short one) being C_2O_2 , CO_2 , and CO . After the carbon has become saturated there is an alternate formation and decomposition of the complex. Each oxygen molecule that impinges on the carbon is at once seized hold of to form the complex, but the energy set free when this occurs decomposes an equivalent proportion of the complex formed from previous oxygen molecules. So that, finally, when air is passed over saturated carbon maintained at a constant temperature by the application of an external source of heat, carbon dioxide and carbon monoxide appear in the products of combustion in volume sufficient to account for the total volume of oxygen in the air originally passed.

In the normal burning of carbon, therefore, the carbon dioxide and carbon monoxide found as the apparently primary products of combustion, arise from the decomposition, at the temperature of combustion, of a complex the formation of which is the first result of the encounters between oxygen and carbon molecules.

The idea of "oxygenation" of the combustible as a preliminary to definite chemical reaction is not without precedent.

The researches of W. A. Bone and his co-workers on the combustion of hydrocarbons point unmistakably to a preliminary *entrance* of the oxygen into the molecule of the combustible, an unstable complex being formed, which breaks up immediately into definite chemical compounds.

Thus, in the case of methane the scheme of reaction is probably:



Formaldehyde has been isolated during the slow combustion of methane over a heated surface and in the flame of methane burning in air, and its presence has been indicated during the propagation of "inflammation" in explosive mixtures of methane and oxygen. Moreover, there is no evidence of any essential difference between the "detonation" and "inflammation" of the paraffins, so far as the result of the *initial* encounters between molecules of hydrocarbon and oxygen is concerned. That is to say, even for the most rapid oxidation, the transitory formation of oxygenated complex may take place.

There seems to us to be nothing to conflict with the supposition that in general it will be found that the initial encounters between oxygen and a combustible material result in the "fixation" of the oxygen, and that the products of combustion that make their appearance are the result of decomposition of a complex first formed. It may be pointed out that the work of Dixon, referred to in a previous paper, on the explosion of the gaseous carbon com-

pounds as exemplified by cyanogen, shows merely that in this case carbon monoxide is produced before carbon dioxide; it does not in any way negative the possibility of the transitory formation of an intermediate combination.

EXPERIMENTAL.

Reference to our previous paper on the combustion of carbon (*loc. cit.*, p. 850) will recall the fact that in determining the rate of oxidation of carbon at different temperatures, great care had to be taken that the carbon surface was in a "normal" condition of activity, such as was obtained after air or oxygen had been circulated over it during a long time at the experimental temperature. In this way alone could the relativity of the results be trusted; for it was noted that when the carbon surface had been subjected to prolonged exhaustion at a high temperature before being brought to the experimental temperature, the rate of disappearance of oxygen at that temperature was abnormally rapid.

As an instance of this we may give the details of an experiment with air at 350°, made after the carbon had been exhausted at a temperature of 950° during several hours.

The rate of disappearance of oxygen is given by the equation:
 $1/t \cdot \log C_0/C_t = k$.

Air over Carbon at 350°. Carbon surface previously exhausted at 950°.

Time.	Po ₂	k (t=1 minute).	Time.	Po ₂	k (t=1 minute)
0	89.0	—	150	67.7	0.00079
15	80.5	0.00291	210	64.0	0.00068
30	77.4	0.00202	270	61.0	0.00061
90	71.3	0.00107	290	56.3	0.00051

It will be seen that the value of k decreases rapidly throughout the experiment, showing a much greater disappearance of oxygen during the first fifteen minutes than over any subsequent period. The "normal" value of k at 350°, which is ultimately attained after several charges of air have been circulated over the carbon surface, is 0.0000546.

It appeared that the rapid fall in pressure in the apparatus during the first few minutes after the air was admitted to the "exhausted" carbon took place before any products of combustion of the carbon could have been carried by the circulating current to the absorption tube for the removal of carbon dioxide. We therefore made a number of experiments in which no attempt was made to remove any carbon dioxide formed, but in which the course of the reaction was followed by the analysis of samples of the gases shut off from the circuit at definite intervals of time (see

diagram, *loc. cit.*, p. 835). A typical example of such an experiment is given below.

Air over Carbon at 400°. Carbon surface previously exhausted at 950°. Carbon dioxide not removed.

Time.	P. mm.	Gas analysis.			P _{CO₂} mm.	P _{O₂} mm.	P _{CO} mm.
		CO ₂	O ₂	CO.			
0	477.4	nil.	20.70	nil.	—	98.9	—
5	469.0	9.10	0.80	4.85	—	—	—
60	465.5	6.10	9.90	2.55	28.3	46.0	11.8
240	463.0	9.65	4.90	3.50	44.7	22.8	16.9
360	461.0	11.00	3.15	3.65	49.6	15.5	18.4

No partial pressures can be calculated from the analysis of the sample taken after five minutes, for it does not, of course, represent the average of the contents of the apparatus. It can be regarded as representing the average composition of the first two or three hundred c.c. of air drawn through the heated carbon. It will be seen that it contained only 0.30 per cent. of oxygen, and that the amount of carbon dioxide and carbon monoxide formed in no way makes up the balance of the oxygen that has disappeared. Moreover, there is a *reduction* of pressure of 8.4 mm., whereas, since the carbon dioxide was not being removed and a certain quantity of carbon monoxide was formed, there should have been an increase.

The samples taken at the end of 60, 240, and 360 minutes more nearly represent the average contents of the apparatus, and the partial pressures of carbon dioxide, oxygen and carbon monoxide calculated from them should be approximately correct. Now, since no product of combustion has been removed, the oxygen-content of the gases in the apparatus, as represented by a sample of the products of combustion at any stage in the experiment, should be the same as that of the air originally introduced. Calculation gives the following results:

Time.	Oxygen content.			Disappearance of oxygen mm.
	CO ₂	O ₂	CO.	
(Original air) 0	nil	+ 98.9	+ nil	= 98.9
60	28.3	+ 46.0	+ $\frac{1}{2}(11.8)$	= 80.2
240	44.7	+ 22.6	+ $\frac{1}{2}(16.9)$	= 75.9
360	49.6	+ 15.5	+ $\frac{1}{2}(18.4)$	= 74.2

As a check on these results calculation can be made of the total reduction in pressure observed in the apparatus at the time the samples were taken; thus, at the end of sixty minutes there was a contraction of 11.9 mm.; but 11.8 mm. of carbon monoxide have been formed, which should have shown an expansion of 5.9 mm. The total contraction observed, therefore, is 17.8 mm., which

compares quite well with the amount of disappearance of oxygen calculated from the gas analysis. Similarly, at times 240 and 360 the total contraction observed was 22.8 and 25.6 mm. respectively.

At the end of three hundred and sixty minutes the circulation was stopped and the reaction-tube exhausted, the temperature being maintained at 400°. The temperature was then rapidly raised to 950°, exhaustion being continuous. Ninety-five and a-half c.c. of gas were evolved from the carbon and collected at the pump. This gas contained:

Carbon dioxide	7.35 per cent.
Oxygen	nil.
Carbon monoxide	91.70.
Nitrogen	0.95 (by difference).

The oxygen-content of this mixture is 53.2 c.c. Since the capacity of the circulation apparatus was 1580 c.c., this corresponds with a pressure of 25.5 mm., which is the total amount of contraction observed during the experiment.

It hardly seemed possible that the exhausted charcoal was capable, when at a temperature of 400°, of occluding or condensing gases in its pores in the same manner as it does at 0°. However, to test this point we made experiments in which the carbon, previously exhausted at 950°, was brought to a temperature of 400°, and treated in the circulation apparatus with (1) carbon dioxide, and (2) carbon monoxide at that temperature. After treatment with each of these gases (during which no absorption of either could be detected), the apparatus was exhausted, the temperature of the carbon being maintained at 400°, and an experiment made with air in the same manner as that recorded above. The result was, in every case, similar to those obtained when the "exhausted" carbon had not been previously treated with carbon dioxide or carbon monoxide at 400°.*

It would appear, therefore, that when oxygen or air is brought into contact at a temperature of 400° with pure carbon which has been freed from all gases by exhaustion at a high temperature, the first thing that happens is a fixation of the oxygen; and that this oxygen cannot be removed as such by exhaustion at 400°, but appears as oxides of carbon when the temperature of the latter is raised.

* For example, in an experiment made after treatment of the surface with carbon dioxide, there was a disappearance of oxygen amounting to 22.6 mm. after 360 minutes' circulation. On raising the temperature to 950°, 88.9 c.c. of gas were evolved containing per cent., CO₂ 6.85; O₂ nil; CO 92.05; N₂ 1.10. The oxygen-content of this gas is 47.1 c.c., which is equivalent to a pressure in the circulation apparatus of 22.9 mm.—the amount of contraction observed during the experiment.

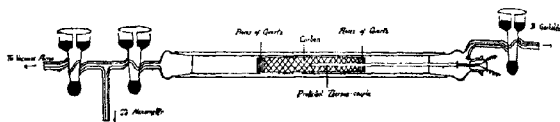
It may be remarked that this fixation of oxygen is effected, not only by charcoal, but also by graphite, although to a less extent.

The Fixation of Oxygen by Carbon.

It appeared that further information regarding what takes place when oxygen is first admitted to heated carbon might be forthcoming from an extended examination of the products of combustion at different temperatures. For this purpose the "circulation" method of experiment was not altogether suitable, for, as a preliminary, we required to obtain some definite idea of the rate of disappearance of oxygen during the first few minutes after its admission to the heated carbon.

The apparatus used for this preliminary series of experiments is shown in Fig. 1. The carbon was packed in a quartz tube 14 cm. long and of 1.6 cm. internal diameter, which just fitted into a

FIG. 1.



porcelain tube 52 cm. long. This porcelain tube had a ground joint at either end, making connexion on the one hand with a gas-holder, and on the other with an automatic Sprengel mercury pump and a mercury manometer. The latter consisted simply of a fairly wide tube of barometric height standing in a trough of mercury.

The porcelain tube was heated in an electric resistance tube-furnace, the temperature of which was maintained constant by means of Nernst lamp resistances in the manner described in previous papers. A platinum and platinum-rhodium thermo-couple passed through a glass plug fitted to one of the end connexions of the porcelain tube (see diagram), the junction being contained in a thin sheath of quartz embedded in the carbon. The temperatures were determined from the deflections of a sensitive "Broca" mirror galvanometer on a scale 40 cm. in length.

The method of experiment was as follows. The apparatus having been thoroughly exhausted with the reaction tube at a temperature of 1000°, the latter was brought to the experimental temperature and the tap leading to the vacuum pump closed. The tap leading to the gas-holder, in which pure oxygen was stored over concentrated sulphuric acid, was then opened during exactly five seconds. At the end of fifteen seconds the first reading of the manometer

was taken,* and from then onwards simultaneous readings were taken of the temperature of the carbon and the pressure in the apparatus at frequent intervals. The initial pressure which should prevail in the apparatus as soon as the oxygen was admitted was calculated from the known volume of the apparatus and the volume of the oxygen used, a preliminary series of experiments with known volumes of nitrogen having been made with the apparatus heated at different temperatures to determine the amount of expansion.

The results can be expressed in tabular form as follows:

Experimental temperature...	300°.			350°.			400°.			500°.			600°.		
Time: minutes.	Pressure, mm.	Temperature.	Percentage contraction.	Pressure, mm.	Temperature.	Percentage contraction.	Pressure, mm.	Temperature.	Percentage contraction.	Pressure, mm.	Temperature.	Percentage contraction.	Pressure, mm.	Temperature.	Percentage contraction.
0-00	734	300°	—	754	350°	—	879	400°	—	702	500°	—	718	600°	—
0-25	587	—	—	622	—	—	744	—	—	682	—	—	687	—	—
0-50	578	380	21-0	611	425	19-0	728	460	17-2	668	540	12-3	671	620	6-9
0-75	565	—	—	604	—	—	721	—	—	659	—	—	667	—	—
1-00	560	—	23-6	598	410	20-7	715	445	18-6	656	535	13-9	665	620	6-7
1-25	556	360	24-2	594	—	21-2	712	415	19-0	654	—	14-1	663	610	7-0
2-25	546	350	25-6	583	400	22-7	—	—	—	647	—	15-0	659	610	7-6
5-25	531	340	27-6	567	380	24-8	685	405	22-1	637	530	16-4	653	605	8-5
15-25	508	—	30-6	539	375	28-5	658	402	25-1	—	—	—	642	605	10-0
30-25	481	320	—	510	360	—	626	400	—	—	—	—	634	605	—
60-25	452	300	—	474	350	—	596	400	—	—	—	—	625	600	—
120-25	429	300	41-4	445	350	41-0	565	400	35-7	590	500	22-6	615	600	13-8

The rate of disappearance of oxygen during the first fifteen seconds is extremely rapid, after which a slow absorption takes place, continuing over several hours.

This is well shown in the curves in Fig. 2. It will be seen that at each temperature the type of curve is the same—the rapid fall in pressure during the first fifteen seconds bearing the same proportion in each case to the total fall at the end of fifteen minutes. The difference between the results at different temperatures would therefore appear to lie, not in the *rate* of fixation of oxygen, but in the *amount* fixed. That is to say, the proportion of the oxygen present that can become fixed at different temperatures becomes so, *ceteris paribus*, in about the same length of time.

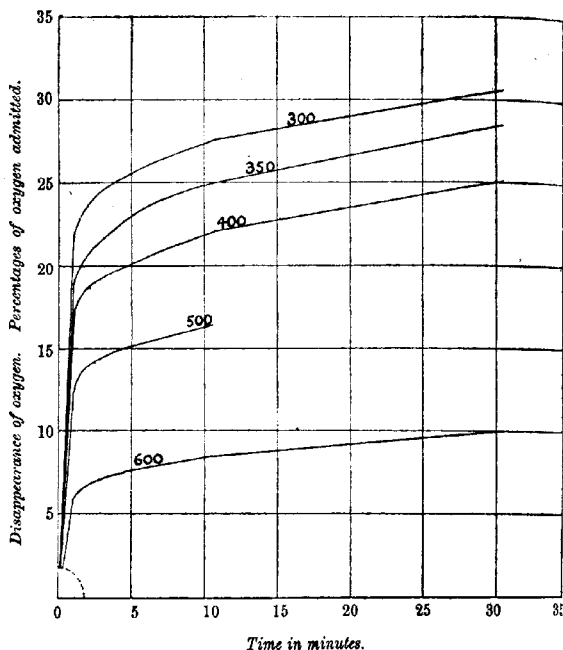
This rather points to a physical explanation of what is taking place; a physical absorption or adsorption of the oxygen, followed, possibly, by chemical change within the carbon. If this were so, however, one would expect that a reduction in pressure alone should suffice to remove either the "absorbed" oxygen or the products of its chemical reaction after absorption; and, if those products are carbon dioxide and carbon monoxide, there seems no reason why the admission of either of these two gases to "ex-

* The oscillations of the mercury in the manometer prevented accurate readings from being made before this time.

hausted" carbon should not result in some absorption of them, at any rate at the lower temperatures.

Such, however, is not the case; we were unable to observe any reduction in pressure in the apparatus when either carbon dioxide or carbon monoxide was admitted to the carbon at a temperature of 250°; nor, on raising the temperature after the apparatus had been exhausted at 250°, were any traces of gas driven off. Moreover, in

FIG. 2.



experiments in which the carbon was treated with either of these gases at 250°, and the apparatus then exhausted at that temperature, the carbon was found to be in the same reactive state towards oxygen as when it had not been so treated.

Another point which may perhaps argue against a physical condensation of oxygen in the pores of the charcoal is the heating effect observed. This, it will be noticed, becomes less pronounced the higher the initial temperature of the carbon. That is to say, the heating effect is less when the proportion of the oxygen admitted that becomes "fixed" is less.

Experiments Regarding the Nature of "Fixed" Oxygen.

The attraction between the oxygen and carbon molecules appeared to be greater than could be explained on the hypothesis that it was a purely physical attraction. We sought, therefore, for some means by which its chemical nature, supposing it partook of such, could be demonstrated.

In the first place it seemed desirable to determine the weight of oxygen that a given weight of carbon would retain at any particular temperature.

A quartz vessel having a narrow inlet-tube for air, that could be closed by a tap of quartz, and a wider exit-tube through which the carbon could be introduced, was loosely filled with 9.7 grams of purified wood charcoal sieved so as to pass through a 60-mesh sieve and remain on a 100-mesh. This bulb was heated in an electric resistance furnace at a temperature of 300° , and dry air slowly drawn through it during six hours. At the end of that time a sample of the gases that passed through was analysed, and since its oxygen-content was found to correspond with that of the air entering, the "fixation" of oxygen was considered to have ceased.

The bulb was then exhausted at a temperature of 300° , the temperature rapidly raised to 1000° , and the gases evolved collected in two portions. The first portion measured (at 0° and 760 mm.) 111.5 c.c., and the second 32.2 c.c. The analyses were:

Volume.	First portion. 111.5 c.c.	Second portion. 32.2 c.c.
Carbon dioxide	22.60	12.15 per cent.
Oxygen	nil.	nil.
Carbon monoxide	76.90	87.35 ,, ,,

The oxygen-content of the whole of the gas collected was, therefore, 85.0 c.c. A repetition of the experiment, using the same weight of carbon, gave the volume of oxygen "fixed" as 88.9 c.c.

The weight of oxygen retained by 12 grams of carbon would therefore be (at 300°) 0.16 gram. That is to say, a formula $C_{100}O$ could be assigned to the combination. This, however, only refers to the particular temperature of 300° .

A definite chemical compound, if it is decomposable at all at one temperature, should be wholly decomposed at that temperature if the products of its decomposition are continuously removed. To be quite certain regarding this point, we made a series of experiments in the apparatus just described, in which the carbon was charged with oxygen at 300° by drawing air through it in a slow stream during two hours. Fractional removal of the gases evolved

on raising the temperature was then made, with the following results:

Temperature of removal of gas.	Volume of gas evolved. C.c.	Analysis.			Oxygen-content. C.c.
		CO ₂	O ₂	CO.	
300—400°	14.0	57.00	nil.	42.35	10.2
400—500	16.7	41.55	"	57.95	10.8
500—600	23.4	30.25	"	69.50	14.0
600—700	32.6	14.55	"	85.00	17.2
700—800	21.3	3.45	"	96.05	10.0
800—1000	36.7	0.75	"	98.70	16.8

The duration of heating and removal of the fractions was six hours at temperatures below 700°; above that temperature it was twelve hours, for minute traces of gas continued to appear at the end of six hours.

These figures, at first sight, seem to negative the idea that the oxygen forms a definite chemical compound with the carbon when it becomes "fixed." It is conceivable, however, that at each fractionation temperature the products of decomposition are carbon dioxide, carbon monoxide, and a third substance which remains undecomposed at that temperature, and is less complicated than the original substance. If this were so, however, every small increment in temperature must be regarded as causing the degradation of one compound and the formation of another, for (as other experiments not detailed here have shown) carbon containing "fixed" oxygen, from which no gas can be extracted at a given temperature, evolves a small quantity of gas when its temperature is raised but a few degrees.

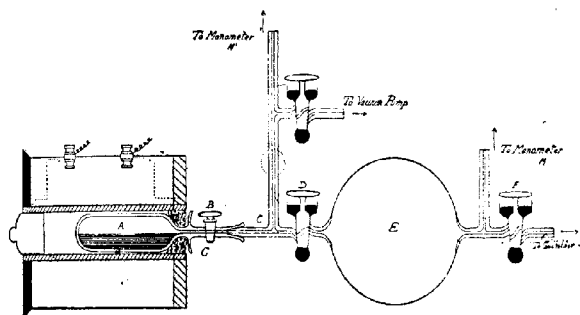
As arguing against a purely physical explanation, on the other hand, it will be noted that the oxygen-content of the gases evolved at different temperature increases up to 700° for every 100° rise in temperature, and then decreases, the greatest evolution taking place between 500° and 700°. This is not what one would expect from a purely physical association of the oxygen with the carbon. In that case, since the quantity of oxygen associated would be a direct function of the temperature, equal increments of temperature should result in regularly decreasing quantities of oxygen evolved.

On the whole, it appears most probable that a loosely-formed complex is formed, to which no definite formula can be assigned, one oxygen molecule (or atom) being held by the attraction, partly chemical and partly physical, of several carbon atoms or molecules. That the oxygen must be partly in the atomic condition seems to follow necessarily from the fact that the decomposition of the complex yields, even at low temperatures, a certain amount of carbon monoxide.

The Distribution of Oxygen between the Products of Combustion of Carbon.

We have already stated that in the experiments just described there was formed, at all temperatures, a certain quantity of the gaseous oxides of carbon as well as the complex during the fixation of oxygen. It seemed to us that considerable information could be obtained from a determination of the proportions in which a known volume of oxygen, when admitted to carbon at different temperatures, appeared in the products of combustion as carbon dioxide, carbon monoxide, and the hypothetical complex, which, for convenience, we will call C_xO_y . For this purpose it was essential that accurate measurements should be made of the volume of oxygen originally admitted to the heated carbon, and of the gases remaining at the end of a definite interval of time. Further, it was

FIG. 3.



necessary that the carbon could be rapidly raised in temperature to 1000° to decompose the complex.

The apparatus used for these experiments is shown in Fig. 3.

The carbon, weighing just under five and a-half grams, was contained in a stout-walled bulb of quartz (*A*), of about 50 c.c. capacity, and occupied about one-third of its volume. This bulb could be closed by a quartz tap (*B*), and was connected by a ground joint to a T-piece (*C*), one branch of which led to a mercury manometer (*M'*) and vacuum pump, and the other, through a mercury-cup tap (*D*) to a globe (*E*) of 649 c.c. capacity. The globe was closed by another mercury-cup tap (*F*), through which it could be filled with oxygen, and was fitted with a mercury manometer (*M*).

The bulb was heated in an electric resistance furnace the refractory tube of which was wound with fine platinum wire, the coils

at the end through which the neck of the bulb passed being placed close together to compensate for loss of heat by radiation from the furnace at that end, which was purposely left unprotected by heat-insulating material. This arrangement enabled a zone of uniform temperature to be obtained throughout that portion of the furnace occupied by the bulb; that is to say, over a distance of 11 cm. starting 4 cm. from the mouth of the furnace.

The quartz tap was kept cold by a rapid stream of water, which was prevented from entering the furnace by a quartz collar (*G*) fused to the neck of the bulb.

Temperatures were measured by means of a platinum and platinum-rhodium thermo-couple passing along the furnace tube, the junction being at *J*, and were maintained constant as before by the use of Nernst steadying-resistances.

Method of Conducting an Experiment.—The whole apparatus having been thoroughly exhausted, with the carbon heated to 1000°, tap *D* and the tap leading to the vacuum pump were closed. The globe *E* was then filled at atmospheric pressure with oxygen from a gas-holder, in which it had been stored for several days over concentrated sulphuric acid.

The carbon was then brought to the experimental temperature, and oxygen admitted to it by rapidly opening tap *D* leading to the globe, and leaving it open during five seconds. The oxygen was heated in contact with the carbon during a given length of time, readings of the manometer *M'* being taken at definite intervals. Tap *B*, leading to the reaction-chamber, was then closed, and the gases contained in the manometer and connexions withdrawn, measured, and analysed separately as "manometer gas." This gas contained, besides unburnt oxygen, a certain quantity of carbon dioxide and carbon monoxide that had diffused from the reaction-chamber.

The gases in the reaction-chamber were then pumped out, exhaustion being continued with the carbon maintained at the experimental temperature during half-an-hour, at the end of which time no further traces of gas appeared.* The volume of these gases was measured and an analysis made ("final gas").

As soon as the "final gas" had been withdrawn, the temperature of the carbon was raised to 1000–1050°, and maintained at that temperature during one hour, exhaustion and collection of the gases evolved being continued throughout. Great care was taken in the comparative experiments that the rate at which the tempera-

* In experiments at temperatures above 800° minute bubbles of gas continued to be removed by the pump at the end of half an-hour, and exhaustion was continued in these cases during one hour.

SERIES I.--Pure Oxygen.

Temperature °C.	100	200	300	350	400	450	500	550	600	650	700	750	800	900
Volume of oxygen burned, c.c.	18.47	32.30	35.84	34.21	27.07	31.47	20.64	17.50	16.18	19.66	16.29	17.88	13.75	11.37
<i>"Manometer Gas."</i>														
Volume c.c.	10.14	8.90	8.35	10.79	11.50	13.76	14.78	16.68	17.29	14.41	14.06	17.25	16.31	18.52
Analysis, CO ₂ per cent.	3.55	4.00	7.45	7.05	6.35	6.30	7.15	5.10	6.80	5.40	4.55	6.00	7.60	10.15
O ₂ "	91.87	89.65	85.90	89.85	89.35	89.85	87.40	90.35	87.50	87.90	91.30	89.80	86.60	77.45
CO "	0.07	1.40	1.90	1.93	0.80	1.15	2.20	1.35	2.70	0.60	0.50	0.35	1.15	5.00
<i>"Final Gas"</i>														
Volume c.c.	33.80	21.95	17.63	17.57	14.55	17.46	11.14	11.07	9.34	13.78	12.06	14.32	13.61	13.22
Analysis, CO ₂ per cent.	9.85	41.96	70.30	73.80	69.60	66.05	68.45	68.45	68.45	83.55	74.30	50.15	8.50	1.50
O ₂ "	64.10	42.80	0.20	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
CO "	0.20	6.85	16.50	19.75	20.25	24.50	29.20	29.56	27.35	12.95	11.65	20.95	45.00	87.85
<i>"C₂O₄ Gas."</i>														
Volume, c.c.	25.00	36.35	35.58	33.29	25.42	29.96	20.08	14.23	11.31	12.91	9.37	8.11	5.00	3.30
Analysis, CO ₂ per cent.	22.00	21.15	16.15	13.20	11.50	10.00	8.75	8.35	5.75	4.55	4.45	3.70	2.00	0.65
CO "	76.40	78.40	82.85	86.80	87.30	89.50	86.70	91.25	92.15	95.00	94.05	96.00	97.60	98.35
Percentage of oxygen burned appearing as:														
(1) CO ₂	19.25	29.60	38.6	39.8	42.3	40.9	40.7	46.2	49.8	61.0	65.9	67.1	55.8	24.6
(2) CO	0.15	2.50	4.3	5.4	5.7	7.0	8.7	10.0	9.9	4.8	4.5	8.8	22.8	60.9
(3) C ₂ O ₄	80.60	67.90	57.1	54.8	52.0	52.1	50.6	43.8	40.3	34.2	29.6	24.1	18.4	14.5

* The last traces of the "Final Gas" at 800°, collected during one hour's exhaustion, were measured and analysed separately, as shown.

* The last traces of the "Final Gas" at 900° collected during one hour's exhaustion, were measured and analysed separately, as shown.

SERIES II.—Oxygen, 50 per cent.; Nitrogen, 50 per cent.

Temperature °C.	300	350	400	450	500	550	600	650	700	800
Volume of oxygen burned, c.c.	14.79	14.76	13.88	12.88	12.41	11.40	10.86	10.35	9.74	8.78
"Final Gas,"										
Volume, c.c.	19.42	19.44	19.70	18.53	19.17	18.30	17.75	16.68	16.12	16.71
Analysis, CO ₂ per cent.	19.35	20.50	20.85	22.30	22.95	23.55	24.35	29.75	31.10	26.55
Analysis, CO ₂ per cent.	nil	0.10	0.10	nil	nil	nil	nil	nil	nil	nil
Analysis, CO ₂ per cent.	3.60	5.20	6.35	7.75	9.90	12.95	14.35	11.00	11.05	20.95
"C ₂ O ₄ Gas,"										
Volume, c.c.	18.49	19.11	16.20	14.42	12.83	11.08	9.98	8.12	7.40	5.05
Analysis, CO ₂ per cent.	15.65	13.95	12.75	11.75	10.35	7.25	6.40	4.75	4.10	2.60
Analysis, CO ₂ per cent.	84.30	85.65	86.95	88.05	89.50	92.30	92.95	94.15	95.80	97.20
Percentage of oxygen burned appearing as: (1) CO ₂	25.4	27.0	29.7	32.1	35.5	37.8	39.8	48.0	51.5	50.6
(2) CO ₂	2.4	3.4	4.5	5.5	7.5	10.4	11.7	8.7	9.1	20.0
(3) C ₂ O ₄	72.2	69.6	65.8	62.4	57.0	51.8	48.5	43.3	39.4	29.4

The duration of heating in each experiment was half an hour.

SERIES III.—Air.

Temperature °C.	200	300	400	450	500	550	600	650	700	800	900
Volume of oxygen burned, c.c.	7.06	6.21	5.60	5.04	4.90	4.00	4.28	3.86	3.55	3.23	2.88
"Final Gas,"											
Volume, c.c.	27.85	24.62	23.05	20.45	20.45	17.56	18.30	17.42	16.74	15.74	16.95
Analysis, CO ₂ per cent.	3.20	4.75	6.00	6.60	7.00	7.35	8.05	8.10	7.35	7.45	1.20
Analysis, CO ₂ per cent.	nil	0.55	1.60	2.75	3.55	4.50	5.45	6.80	8.70	11.25	23.55
"C ₂ O ₄ Gas,"											
Volume, c.c.	10.46	8.65	7.28	6.65	5.92	4.54	4.34	3.69	2.96	2.28	1.56
Analysis, CO ₂ per cent.	18.45	13.35	11.35	8.40	7.65	7.55	8.05	8.65	8.65	8.65	0.15
Analysis, CO ₂ per cent.	81.20	84.40	88.20	86.10	80.05	91.05	95.95	95.95	97.55	99.05	99.70
Percentage of oxygen burned appearing as: (1) CO ₂	12.6	18.8	24.7	26.8	29.2	31.8	35.6	36.5	37.0	37.3	6.8
(2) CO ₂	—	1.0	3.1	5.5	7.3	9.6	11.8	15.3	20.7	27.3	68.1
(3) C ₂ O ₄	87.4	80.2	72.2	67.7	63.6	58.6	52.6	48.2	42.3	35.6	27.1

The duration of heating in each experiment was a quarter of an hour. No oxygen could be detected in any of the samples of "Final Gas."

ture was raised from the experimental temperature to 1050° should be the same in each case, and that that rate should be rapid. This was effected by suddenly increasing the voltage of the current passing through the furnace to 200, maintaining that voltage until a temperature of about 1050° was reached, and then lowering it to 130. In this way the temperature of the furnace could be raised from 300° to 1050° in under ten minutes, and the latter temperature maintained without any serious fluctuations. The gas removed in this manner was measured and analysed as " C_2O_2 gas."

The results of the experiments are given in the table that follows. The volumes of "oxygen burned" are calculated from the total oxygen-content of the carbon dioxide and carbon monoxide in the "manometer," "final," and " C_2O_2 " gases. All volumes are reduced to 0° and 760 mm. The duration of heating in each experiment was one hour.

At temperatures above 900° it was difficult to decide whether any oxygen became "fixed." Prolonged exhaustion at the experimental temperature continued to remove traces of gas until the whole of the oxygen admitted to the carbon could be accounted for as carbon dioxide and carbon monoxide. On the other hand, the last traces removed in this manner were very different in composition from the main bulk of the "final gas," and it seems likely that at temperatures above 900° reduction in pressure alone is sufficient to cause the decomposition of the complex.

Two further series of experiments were made, one with a mixture of equal volumes of oxygen and nitrogen, and the other with air. The form of apparatus used was simplified for these two series, the gases being delivered under pressure to the reaction-vessel from a graduated holder (made from a 50 c.c. standard burette graduated in tenths of a c.c.), and no manometer being employed.

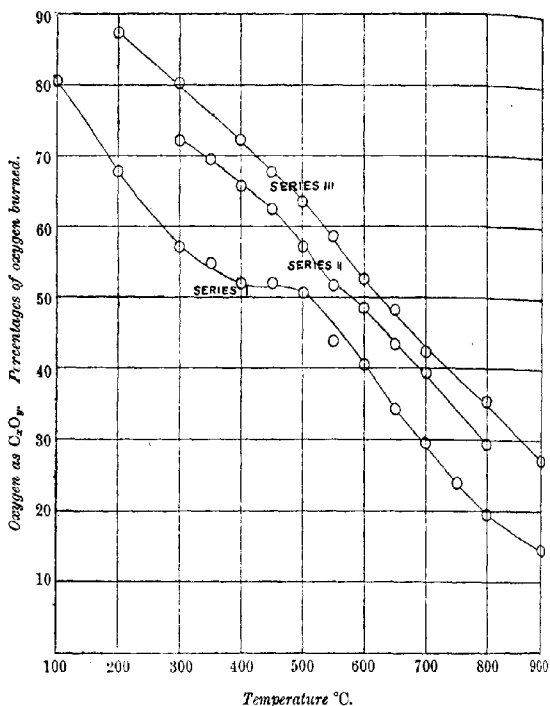
Although, owing to the dilution with nitrogen, rather small quantities of oxygen were used in each experiment, the volumes could be measured very accurately, and good agreement was always obtained between the volume of oxygen admitted to the carbon, as measured directly from the supply-burette, and the total oxygen-content of the "final gas" and the " C_2O_2 gas."

The curves in Fig. 4, prepared from the above three series of experiments, show the variation with temperature in the percentage of the oxygen burned that forms the complex C_2O_2 , when a limited supply of oxygen is admitted to "exhausted" carbon.

When less oxygen is admitted to exhausted carbon than is sufficient to saturate it at the temperature employed, it becomes fixed very rapidly; and we imagine that if no heating effect took place all the oxygen admitted would become so fixed. A very slight

increase in temperature is, however, sufficient to liberate some of the fixed oxygen as carbon dioxide and carbon monoxide. A certain proportion of the oxygen admitted, therefore, appears in the products of combustion as these gases. The percentage that thus appears depends on the heating effect produced; that is to say, it

FIG. 4.



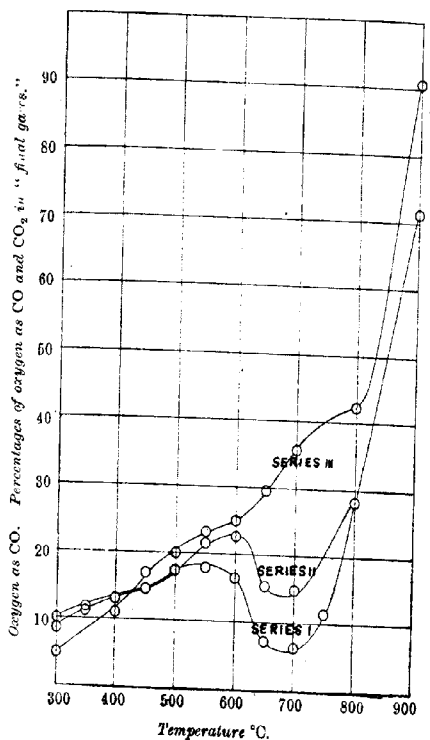
depends on the original temperature of the carbon and on the concentration of the oxygen.

This is apparent on comparing the curves in Fig. 5. The smaller the concentration of the oxygen at any one temperature the larger the percentage of the oxygen burned that forms what we have assumed to be a physico-chemical complex, C_2O_4 .

Taking the curve for pure oxygen (Series I), it will be seen that even at 900° as much as 14 per cent. of the oxygen burned forms the complex. The percentage does not increase regularly with

decreasing temperature, but, when 500° is reached, remains fairly constant until 400° , after which the curve resumes its former inclination. Another similar series of experiments with pure oxygen (not recorded in this paper), in which the volume admitted was in excess of that required to saturate the carbon, showed a similar break in the curve for formation of C_xO_y over the range

FIG. 5.



$50-500^{\circ}$. The curve for "50 per cent." oxygen also shows a slight break at about 450° , that for air practically none.

We cannot at present assign any definite meaning to this break in the curve, unless it be that at temperatures between 400° and 600° the complex or series of complexes presumed to be formed have greater stability than at higher or lower temperatures. That should appear but slightly defined in the curves for air and

50 per cent. oxygen is understandable for the reason that in these two series of experiments the volume of oxygen used was greatly in defect of that required for complete saturation of the carbon; whilst we have already seen that at all temperatures the rate of formation of the complex is about equally rapid; it is only the amount formed that varies.

Let us now turn our attention to the percentages of carbon dioxide and carbon monoxide produced apparently simultaneously with the complex. The percentage of the oxygen burned that appears as the gaseous oxides of carbon increases with increased temperature of the carbon. What we are more concerned with is the relationship between the amounts of these two oxides produced at different temperatures.

This relationship is best brought out by considering the oxygen content of the "final gas," apart altogether from that of the complex. We have therefore calculated the percentages of the oxygen burned that appear as carbon dioxide and carbon monoxide in the "final gases" as percentages of the sum of the two.

The figures thus obtained are given in the table that follows, whilst Fig. 5 shows the curves for oxygen as carbon monoxide obtained from these figures.

Oxygen as CO. Per cent. of Total Oxygen as CO₂ and CO in "Final Gases."

Temperature.	Series I.	Series II.	Series III.
300°	9.9	8.6	5.0
350	11.8	11.1	—
400	11.7	13.1	11.1
450	14.7	14.6	17.0
500	17.4	17.4	20.0
550	17.7	21.6	23.2
600	16.5	22.7	24.9
650	7.2	15.3	29.6
700	6.3	15.0	35.8
750	11.6	—	—
800	28.1	23.3	42.2
900	71.2	—	90.6

Taking the curve for pure oxygen (Series I) first, it will be seen that the percentage of the oxygen that appears as carbon monoxide increases fairly regularly until a temperature of about 550° is reached; it then decreases rapidly, to increase again at temperatures above 750°.

Until a temperature of 550° is attained the rate of the reaction $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ is slow. Moreover, the occurrence of this reaction presumes the presence of an excess of oxygen for a certain length of time, whereas the volume of oxygen used in each experiment is in defect of that required for the formation of the total amount of

the complex that can be formed with the weight of carbon used. Such oxidation of carbon monoxide molecules as takes place at these lower temperatures must therefore occur during the interval between the breaking up (owing to local heating) of some of the complex formed during the initial encounters between the oxygen molecules and the carbon, and the complete using up of the oxygen; a space of time which, owing to the rapidity of the reaction responsible for the formation of the complex, is not very great. Between 550° and 700°, however, the rate of oxidation of carbon monoxide rapidly increases, whilst the amount of oxygen rapidly removed to form the complex is not so great. A certain amount of carbon monoxide is thus capable of being oxidised before all the oxygen is removed from the sphere of action.

Finally, at temperatures above 750° the rate of the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$ begins to be appreciable, and the quantity of carbon dioxide reduced at these higher temperatures depends largely, of course, on the length of time it is allowed to remain in contact with the carbon.

The curve for Series II (50 per cent. oxygen) is similar to that of Series I, but in this case a temperature of 600° has to be reached before the reaction $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ begins to predominate.*

When air is used (Series III), the percentage of the oxygen burnt that appears as carbon monoxide in the final gases increases regularly up to 750° (when reduction of carbon dioxide begins to take place to an appreciable extent), no excess of oxygen being left sufficiently long at any temperature to oxidise the carbon monoxide to any great extent as it arises from decomposition of the complex.

It will be noticed that at temperatures below 450° the curve for the experiments with air passes beneath the curves for the series containing the larger percentages of oxygen. This is quite in accordance with the supposition that both the carbon dioxide and the carbon monoxide found in the "final gases" arise from decomposition of part of the complex first formed; for the decomposition when the higher concentrations of oxygen were present would take place at a slightly higher temperature—the encounters between

* A series of experiments was made in a similar manner to the above with a mixture of carbon monoxide and oxygen containing 20 per cent. of carbon monoxide. The results showed that below 650° the rate of formation of carbon monoxide from the carbon was more rapid than the rate of oxidation of the carbon monoxide present in the original mixture; but that above that temperature the reverse was the case. Thus, the volumes of oxygen that entered the reaction-chamber as carbon monoxide, and the volumes found in the "final gases" were:

Temperature.	400°	500°	550°	600°	625°	650°
Oxygen as CO in original gas, c.c.	2.86	2.17	2.67	1.94	2.10	1.75
Oxygen as CO in final gas, c.c., ...	3.53	3.29	3.40	3.53	4.18	0.90
Difference, c.c.,	+0.72	+1.12	+1.33	+1.59	+2.18	-0.85

the oxygen molecules and the carbon being more frequent—and we have shown that the higher the temperature of decomposition of the complex the lower the ratio CO_2/CO in the gases evolved.

If our conception of what takes place is correct, these ratios CO_2/CO in the experiments just recorded (Series III) should represent, at any rate for the lower temperatures, approximately the ratios in which the gases should make their appearance when a stream of air is passed over "saturated" carbon at corresponding temperatures. For we have shown that the volume of oxygen used in the experiments with air was so much in defect of that required to saturate the carbon, that the proportion of carbon monoxide found in the "final gases" can be regarded as having undergone but little diminution owing to oxidation by excess of oxygen; and that, therefore, the ratio in which carbon dioxide and carbon monoxide were found represents approximately at each temperature the ratio in which they arose from decomposition of the complex.

To put this hypothesis to the test, we have made a large number of experiments, in which "saturated" carbon was heated at different temperatures in streams of air and of oxygen at varying velocities. A sufficient number of data were obtained to enable us to eliminate the effects due to local heating of the carbon, or to subsequent interaction of the products of combustion and excess of either oxygen or carbon.

Experiments with "Saturated" Carbon.

In distinguishing between exhausted and saturated carbon we have not intended to imply that there is any essential difference in their *mode* of combustion. The difference between what happens when oxygen is admitted to one or the other at a given temperature is, according to our hypothesis, simply that in the first case most of the oxygen molecules that encounter the carbon are permanently detained; whilst in the second case the detention is merely momentary. The exhausted carbon continues to detain oxygen molecules permanently until it becomes saturated.

In the experiments with *saturated* carbon at different temperatures now to be described dry air was drawn through the carbon, maintained at the experimental temperature, until the exit gases contained the proper oxygen-content for air. The carbon was then regarded as saturated at the experimental temperature. A measured volume of air (or oxygen) was then drawn at a constant speed through the carbon by means of a Sprengel mercury pump, and the whole of the products of combustion collected over mercury in

a graduated reservoir. The "reaction-vessel" employed was a porcelain tube of 2 cm. internal diameter and 52 cm. long, into which a short, thin-walled tube of quartz containing the carbon just fitted, and was placed so as to occupy a central position.

Considerable difficulty was experienced in saturating the carbon and maintaining it saturated at the experimental temperature. Any accidental lowering in temperature after saturation had been completed rendered the carbon capable of causing the fixation of a further quantity of oxygen, and so caused a deficit in the oxygen-content of the issuing gases. It was found best, therefore, not to attempt to obtain as "experimental temperatures" for this series the even hundreds, 400°, 500°, etc., as had been done in previous series, but to get as near these values as possible by using a constant voltage of the electric current through the furnace, as near as possible to that which had previously been found to give the required temperature.

At temperatures above 550° a further difficulty arose in that the heat of the reaction caused a marked rise in the temperature of the carbon, and this rise in temperature was greater the more rapid the passage of the air current. To overcome this difficulty it was found necessary to continue the passage of the air-current at the velocity required for some little time before taking a sample of the issuing gases, the result being that for a given "experimental temperature" the *actual* temperature of the carbon varied with the velocity of the air-current.

The experimental temperature (as indicated by a thermo-couple embedded in the carbon) was measured at the outset of an experiment by the readings of a recording galvanometer giving a deflection of about 1 cm. per 100°. The "actual" temperatures were obtained during the course of the experiments from the deflection of a spot of light thrown by a "Broca" mirror galvanometer on a scale 40 cm. long. The resistance of the galvanometer was such that 3.66 millimetre divisions on the scale were equivalent to 1°. The zero of this instrument was set in each experiment at the "experimental temperature," so that the deflection observed showed at once the heating effect of the reaction.

As an example, to make the operation clear, we give the details of a series of experiments made at an experimental temperature of 640°. The carbon having been saturated at 640°, the first experiment of the series was made with a rapid current of air.

The velocity of the air-current was adjusted so as to be approximately 100 c.c. per minute. As soon as the stream was started the temperature of the carbon rose, the readings of the galvanometer being:

Time, minutes.	Deflection of galvanometer. mm.	
0	0	"Experimental temperature," namely, 640°.
1	52	
2	63	
3	68	
4	71	
5	72	
10	74	= +20°
15	74	
20	74	The sample of the issuing gases was taken during this period.
25	74	

The actual temperature was therefore 660°. The carbon was now allowed to regain the experimental temperature, and a stream of air of 100 c.c. in 2.3 minutes passed. A maximum deflection of the galvanometer equivalent to 37 mm. on the scale was produced. The "actual" temperature in this experiment was therefore 630°.

Similarly, with streams of 100 c.c. in 6.5 and 16.2 minutes the deflections observed were 4 mm. and 0 mm. respectively; the heating effect of the reaction could therefore be neglected in these two experiments.

In the table that follows each series of experiments is headed by the "experimental temperature." The "actual temperatures" are recorded in separate columns in each series. The other data given are:

(1) The number of the experiment, showing the order in which the different velocities of air-current were obtained. This is sometimes of importance when considering the general nature of the results of each series.

(2) The velocity of the air-current expressed as times of collection of 100 c.c.

(3) The analyses of the samples of the products of combustion.

(4) The ratios CO_2/CO in the analyses.

(5) The proportions of the oxygen burned appearing as carbon monoxide.

(6) The percentage "oxygen-content" of the air burnt, calculated from the products of combustion. This should be about 20.9.

Actual tempera- ture. °C.	Expt. No.	Time of collec- tion of 100 c.c. Mins.	Ana'lysis, per cent.			Ratio CO ₂ /CO.	Oxygen as CO, (Calculated) per cent. of oxygen burned.	Oxygen-con- tent of air, from the products of combustion.
			CO ₂ .	O ₂ .	CO.			
<i>Experimental Temperature 400°.</i>								
400	5	1.5	1.00	19.40	0.25	4.00	10.70	20.6
400	1	4.0	4.65	17.20	1.40	3.30	18.10	22.3
400	2	8.1	5.10	14.85	1.70	3.00	14.30	20.9
400	4	13.1	6.50	12.45	2.60	2.60	16.65	20.5
400		14.7	7.50	11.30	3.30	2.25	18.05	20.8

Actual tempera- ture, °C.	Expt. No.	Time of collection of 100 c.c. Mins.	Analysis, per cent.			Ratio CO ₂ /CO.	Oxygen as CO, per cent. of oxygen burned.	Oxygen-con- tent of air, (Calculated) from the products of combustion.
			CO ₂ .	O ₂ .	CO.			
<i>Experimental Temperature 425°.</i>								
425	3	2.2	5.00	13.90	1.85	2.70	15.55	20.0
425	1	4.9	9.70	7.20	4.45	2.20	18.60	19.6
425	2	10.6	11.90	4.40	5.70	2.10	19.30	19.7
425	4	15.2	13.30	2.70	6.10	2.20	18.65	19.7
<i>Experimental Temperature 535°.</i>								
560	1	2.7	14.10	trace	10.55	1.35	27.20	20.4
550	2	8.4	15.30	nil	9.85	1.55	24.30	20.4
545	3	12.0	15.55	nil	9.60	1.60	23.60	21.3
540	4	17.2	15.95	nil	9.85	1.60	23.60	21.6
<i>Experimental Temperature 570°.</i>								
590	1	0.45	10.80	1.25	13.85	0.80	33.20	20.1
580	2	2.9	13.70	nil	13.05	1.05	32.25	21.6
575	3	8.0	15.25	nil	11.60	1.30	27.55	22.3
570	4	14.5	15.85	nil	10.00	1.60	24.00	21.9
<i>Experimental Temperature 600°.</i>								
630	4	1.7	12.25	nil	15.80	0.80	39.20	21.8
610	2	7.9	14.05	nil	14.05	1.00	33.30	22.7
600	3	12.1	14.10	nil	12.95	1.10	31.45	22.0
600	1	28.4	15.85	nil	13.15	1.20	29.30	24.0
<i>Experimental Temperature 650°.</i>								
680	1	1.4	11.70	nil	14.65	0.80	38.50	20.5
670	2	2.3	12.05	nil	13.60	0.90	36.05	21.0
655	3	6.5	13.10	nil	13.60	0.95	34.20	21.3
650	4	16.2	14.25	nil	11.80	1.20	29.30	21.4
<i>Experimental Temperature 700°.</i>								
725	1	0.9	12.15	trace	13.90	0.90	36.30	20.6
710	3	4.2	14.20	nil	11.65	1.20	28.80	21.2
705	2	11.0	15.65	nil	8.75	1.80	21.60	20.9
705	4	21.0	16.70	nil	7.70	2.20	18.75	21.3
<i>Experimental Temperature 770°.</i>								
780	1	1.3	19.00	nil	3.25	5.85	7.85	20.9
770	2	6.9	17.45	nil	5.70	3.05	14.00	20.9
770	3	14.5	17.50	nil	5.60	3.10	13.80	20.9
770	4	28.4	17.60	nil	4.60	3.80	11.55	20.4
<i>Experimental Temperature 840°.</i>								
860	1	1.3	19.25	nil	2.80	6.90	6.80	20.9
845	2	5.3	19.10	nil	3.15	6.05	7.60	21.0
840	3	9.5	19.30	nil	2.90	6.65	7.00	21.0
840	4	25.0	19.40	nil	2.90	6.70	6.95	21.0
<i>Experimental Temperature 910°.</i>								
915	1	0.8	18.85	nil	2.50	7.55	6.20	20.3
915	2	4.5	17.15	nil	5.00	3.45	12.70	20.2
910	3	13.7	16.30	nil	7.00	2.35	17.70	20.5
910	4	35.2	15.45	nil	8.50	1.80	21.55	20.6
<i>Experimental Temperature 1000°.</i>								
1005	1	1.3	13.85	nil	11.35	1.20	29.80	20.1
1000	2	11.0	5.00	nil	25.00	0.20	71.55	20.0
1000	3	24.5	2.2	nil	29.95	0.05	86.95	20.3

These results considered together afford a very fair idea of the sequence of events when air is passed in a stream through heated carbon.* For their better comprehension the curves in Fig. 6

* There are several points in connexion with these results which require explanation.

At 400° the ratio CO_2/CO decreases regularly with decreasing speed of air-current. That is to say, the proportion of the oxygen burnt that appears as carbon monoxide is greater the slower the air-stream. This we presume to indicate the influence of local heating of the carbon. Any local heating would cause more rapid oxidation of carbon monoxide by excess of oxygen at those temperatures where excess of oxygen could remain in the gases for an appreciable time, namely, at temperatures below 500°. Its effects would be more apparent at those temperatures where the more rapid stream of air; for, as with the general heating effect, the local heating effect must be more intense the more rapid the air-current. In those experiments, therefore, where the general temperature of the carbon surface was insufficient to cause the rapid oxidation of carbon monoxide, a slow stream would yield a greater proportion of carbon monoxide than a fast stream. A very slow stream, or a slightly higher general temperature of the carbon, might occasion the oxidation of an appreciable quantity of carbon monoxide.

This contention is borne out by the results of the experiments at 425°, in which the proportion of the oxygen burnt that appears as carbon monoxide increases with decreasing rapidity of air-current up to a certain point, and then decreases. The explanation is that the slowest rate of passage of air in this series of experiments afforded time enough for the oxidation of carbon monoxide as it passed with excess of oxygen over the carbon surface, the general temperature of which was 425°.

At temperatures between 500° and 700° the ratio of CO_2/CO in the products of combustion increases with decreasing velocity of air-current. At these temperatures the rate of oxidation of carbon monoxide is rapid, and the increased time of contact between the products of combustion (containing excess of oxygen) over the carbon surface afforded by slow streams, more than compensates for the diminution in the degree of local heating in its effect on the oxidation of carbon monoxide.

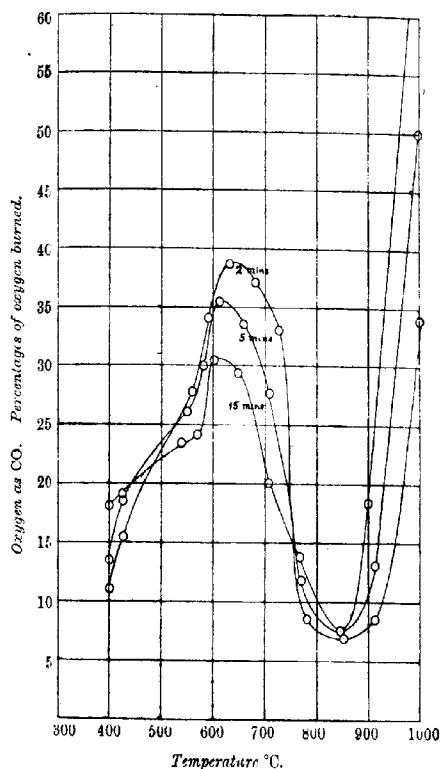
Above 850° the rate of the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$ becomes appreciable, its effects being, as might be expected, more marked the slower the stream of air. It is interesting to note that even with the slowest stream at 1000° equilibrium of the system $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$ was not attained.

We may remark that all these results have been confirmed by duplicate series of experiments.

There is a further point in connexion with these experiments to which attention should be drawn, namely, the variations in the oxygen-content of the products of combustion. Allowing for the increase in volume due to the formation of carbon monoxide, the oxygen-content of the original air passed can be calculated. It should be about 20.9. The fact that in many cases a greater and in some cases a smaller percentage was found emphasises what we have already said regarding the difficulty of maintaining the carbon "saturated" at the experimental temperature. We are satisfied that the fluctuations in the oxygen-contents observed are not due to experimental error—we believe that the determinations of the constituents of the products of combustion are correct within 0.05 per cent.—and it will be observed that there is a certain regularity amongst them, each series at a particular experimental temperature yielding a uniformly high or low result as the case may be. The high results we attribute to excessive decomposition of the complex, due to the heat of the reaction; the low results to insufficient saturation of the carbon before collection of the samples was made.

have been plotted. These curves represent the percentages of the oxygen burnt that appear in the products of combustion as carbon monoxide at different temperatures, with speeds of air-current yielding 100 c.c. in 2, 5, and 15 minutes respectively. The percentages for these speeds are interpolated from the experimental numbers, the temperatures being to the nearest 5 degrees.

FIG. 6.



The temperatures at which the reactions $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ and $\text{CO}_2 + \text{C} = 2\text{CO}$ are most prominent can readily be seen from these curves. We are most concerned, however, with the curve for temperatures below 650°, at which temperature the percentage of oxygen as carbon monoxide reaches its maximum with the most rapid air-current; for below this temperature, with rapid air-

currents, the effects of reactions subsequent to the oxidation of carbon do not predominate.

If from the curve for the most rapid air-current the percentages of oxygen as carbon monoxide at temperatures of 400°, 450°, 500°, 550°, 600°, and 650° be taken, the ratio CO_2/CO in the products of combustion at these temperatures can be calculated, and comparison made with the ratios obtained in the "fixation" experiments with air. In these latter experiments, it will be remembered, it was concluded that the percentages of carbon dioxide and carbon monoxide found at the end of a quarter of an hour's heating could be regarded as approximately those in which the gases were liberated by decomposition of the complex, at any rate at temperatures below 500°. For at these temperatures the small quantity of oxygen used in the experiments was removed so quickly from the sphere of action as to preclude the possibility of much secondary oxidation of carbon monoxide, the rate of that reaction being slow. Between 500° and 700°, however, it appeared probable, from a consideration of the results obtained from similar experiments with pure oxygen and "50 per cent." oxygen, that some secondary oxidation took place in the time. The ratio CO_2/CO would therefore be too high at these temperatures.

We give below the results obtained for the ratio in the rapid "stream" experiments just described, together with those in the "fixation" experiments with air:

Temperature.	Ratio CO_2/CO in products of combustion.	
	"Stream" experiments.	"Fixation" experiments. (Series III.)
400°	3.80	3.75
450	2.28	2.40
500	1.70	1.97
550	1.35	1.63
600	0.90	1.48
650	0.73	1.19

It will be seen that the results are of the same order, the ratio decreasing with increasing temperature; and that at temperatures below 550° there is a fair agreement between the two sets of ratios. Above that temperature, as anticipated, the "fixation" experiments show a higher ratio than the "stream" experiments, due, no doubt, to subsequent oxidation of carbon monoxide, the extent of which would be minimised in the rapid stream experiments.

On the one hand, therefore, we have a set of ratios CO_2/CO in the products of combustion obtained during the oxidation of "saturated" or "normal" carbon in a stream of air; and on the other hand a similar set of ratios obtained during the "fixation" of oxygen by "exhausted" carbon, when the major portion of the

oxygen burnt is retained by the carbon to form (presumably) a carbon-oxygen complex, such oxygen as appears in the gaseous products of combustion being due to the decomposition of this complex. The two sets of ratios show considerable concordance. The hypothesis is that in the normal burning of carbon the carbon dioxide and carbon monoxide found as the apparently primary products of combustion arise from the decomposition, at the temperature of combustion, of a complex, the formation of which is the first result of the encounters between oxygen and carbon molecules.

Our thanks are due to the Explosions in Mines Committee of the Home Office for permission to publish these results.

We wish, also, to express our appreciation of Professor Bone's kindness in communicating this paper to the Society.

ESKMEALS.

LIV.—*Existence of Racemic Compounds in the Liquid State.*

By ALEC DUNCAN MITCHELL and CLARENCE SMITH.

DURING the past twenty years various physical properties of liquids have been utilised in an attack on the problem of the existence of racemic compounds in the liquid state, but the change of the molecular surface energy with temperature appears not to have been applied until Gróh a few months ago (*Ber.*, 1912, **45**, 1441) recorded the result of two experiments on dimethyl tartrate and dimethyl racemate.

A survey of the results obtained by different investigators, a summary of which can be found in recent papers on this subject by Dunstan and Thole (*T.*, 1908, **93**, 1815; 1910, **97**, 1249; this vol., p. 19) leaves on the mind the impression that the existence in the liquid state of a racemic compound of two enantio-stereoisomerides has not been definitely and satisfactorily established. Several investigators assert that liquid racemates do exist, but the weight such statements carry is a matter of opinion, in view of the uncertain quantitative value of most of the methods by which the problem has been treated. Methods based on the determination of the density or of the refractive index (Traube, *Ber.*, 1896, **29**, 1394; Pope and Peachey, *T.*, 1899, **75**, 1111), by which therefore the greatest accuracy can be attained, definitely deny the existence of racemic compounds in unassociated liquids.

Ramsay and Shields have shown (*Phil. Trans.*, 1893, **184**, 647) how the molecular weight of a pure unassociated liquid can be determined from the rate of change of the molecular surface energy with temperature; for such liquids the relation between the change and the temperature is linear, except in the neighbourhood of the critical point, and the rate of change is a constant, k , the average value of which, determined by six "normal" liquids, is 2.1209. Before the application of this method to the problem of the existence of liquid racemates is described, some discussion of the significance of the constant k is necessary. The average value, 2.1209, is the mean of six lying between 2.2256 for ethyl acetate and 2.0419 for methyl formate. Values even greater than the former have been recorded in recent years by Hewitt and Winmill (*T.*, 1907, **91**, 441), Turner and Merry (*ibid.*, 1910, **97**, 2069), Walden and Swinne (*Zeitsch. physikal. Chem.*, 1912, **79**, 700), and others. The criterion of the unaltered molecular complexity of a liquid with change of temperature is not so much the absolute value of k , as its constancy. When the liquid is unassociated, k remains the same over a wide range of temperature, but in the case of an associated liquid the dissociation which accompanies rise of temperature is manifested by a rapid increase in the value of k . Thus, for ethyl alcohol and for glacial acetic acid, k has the values 1.070 and 0.8815 respectively at 20° and 1.569 and 1.198 respectively at 150°.

The application of this method to the problem under examination is as follows. The surface tensions and the densities of each of the optically active modifications of a substance are determined over as wide a range of temperature as is practically convenient, and thereby, assuming a normal molecular weight for the substance, several values of k are obtained by the equation

$$k = \frac{\delta[\gamma(Mv)^{\frac{2}{3}}]}{\delta t},$$

and the mean is calculated.

The same measurements are made with the inactive modification, and the mean value of k' is determined, again assuming a normal molecular weight for the substance. If this assumption is correct, that is, if the inactive modification is a liquid mixture of the two active forms, the mean values of k and k' will be identical or nearly so. On the other hand, if the inactive substance is a liquid racemic compound, and therefore has twice the molecular weight of the active modifications, k' will be smaller than k , the two quantities being related by the equation $k = 2k'$. Finally, the inactive liquid may be a mixture of the two active forms in equilibrium with the racemic compound. In this case k will the more exceed k' the greater the amount of the racemic compound present, a change of

0.01 in the value of k' corresponding roughly with a change of about 0.7 per cent. in the molecular weight. (Strictly speaking, the name "molecular weight" is inapplicable to such a liquid; its meaning, however, is obvious, and the name will be retained to avoid circumlocution.)

There remains to be considered the question of the association, other than the chemical combination, of the liquid molecules. This complication has been avoided by selecting for examination substances which the experience of previous workers has shown are little prone to association, namely, hydrocarbons and esters. The active and the inactive modifications of pinene and of limonene, and dimethyl *d*-tartrate and dimethyl racemate have been examined. The concordant values of k for the active and the inactive modifications of each substance and its constancy over a wide range of temperature prove that the substances selected fulfilled expectation, and that the results are not complicated by changes due to ordinary association.

EXPERIMENTAL.

The apparatus and the general mode of procedure for the determinations of the surface tension at different temperatures were similar to those described by Hewitt and Winnill (*loc. cit.*). All measurements of length were made with a vernier microscope reading directly to 0.01 mm., and by means of a micrometer eye-piece to 0.001 mm. Many capillary tubes were tested until one was found with a uniform bore over a length of 5–6 cm. This was then sealed to the wide tube of the apparatus, so that the surface of the liquid within the capillary was always situated within the uniform portion. The usual precautions were observed of thoroughly wetting the capillary walls and of determining the surface tension of the liquid in contact with its own vapour. The diameter of the uniform part of the capillary tube was determined by direct measurement with the micrometer eye-piece, by calibration with a mercury thread, and by a determination of the surface tension of benzene; the three methods gave practically identical results.

The densities of the liquids at different temperatures were determined by means of a dilatometer consisting of a cylindrical bulb of about 9 c.c. capacity sealed to a capillary tube, in which six or seven small bulbs, of about 0.04 c.c. capacity, were blown at intervals of about 2.5 cm. File marks were made on the capillary stem between the small bulbs. The dilatometer with the bulb completely filled with the liquid under examination was immersed in a large bath of water or other liquid heated by a small flame.

The temperatures to 0.1° were noted at which the liquid surface coincided with the various file marks on the capillary stem. The dilatometer was calibrated by a series of readings with water. This method of determining the densities of a liquid at different temperatures was devised by Mr. T. F. Winmill. It is very convenient and accurate. After the densities of benzene at different temperatures between 15° and 75° had been determined, it was found that the results agreed to 0.0001 with those obtained by Walden (*Zeitsch. physikal. Chem.*, 1909, 65, 129).

The values of h recorded are obtained from smoothed curves of the experimental values.

Pinene.

d-Pinene.—The liquid, after repeated fractionation under diminished pressure, boiled at $85^\circ/80$ mm., and had $[\alpha]_D^{25}$ 13.4° .

l-Pinene.—Purified in a similar manner. Boiling point $70.5^\circ/35$ mm.; $[\alpha]_D^{25}$ -22.0° .

i-Pinene.—Sample I. Prepared from pinene nitrosochloride by Wallach's method. Boiling point 156° . Optically inactive. In the experiments, it became slightly yellow after keeping for some time at the higher temperatures, but after cooling, the surface tension was found to be unchanged.

Sample II. Prepared by mixing *d*- and *l*-pinenes to produce an optically inactive liquid.

d-Pinene. $M=136$. $r=0.02790$.

t .	d .	h .	γ .	$\gamma(Mv)^{1/2}$.		$k_{(124-4)}$.
12.6	0.8686	2.292	27.23	790.9	$k_{(124-62.7)}=2.38$	—
23.8	0.8592	2.222	26.11	764.0		2.40
35.9	0.8491	2.146	24.93	735.4	$k_{(23.8-71.7)}=2.37$	2.38
49.8	0.8378	2.058	23.60	702.3		2.38
62.0	0.8277	1.983	22.45	673.4	$k_{(35.9-82.7)}=2.35$	2.38
71.0	0.8202	1.927	21.61	652.1		2.38
82.5	0.8106	1.856	20.58	625.9	$k_{(49.8-91.4)}=2.33$	2.36
91.4	0.8032	1.801	19.79	605.5		2.35
Mean = 2.36						2.37

l-Pinene. $M=136$. $r=0.02790$.

t .	d .	h .	γ .	$\gamma(Mv)^{1/2}$.		$k_{(114-4)}$.
11.4	0.8709	2.290	27.27	790.8	$k_{(11.4-58.9)}=2.36$	—
20.9	0.8630	2.229	26.32	767.7		2.43
34.3	0.8519	2.147	25.03	736.3	$k_{(20.9-60.7)}=2.33$	2.38
47.7	0.8410	2.064	23.74	704.6		2.37
58.8	0.8317	1.996	22.71	679.0	$k_{(34.3-70.7)}=2.33$	2.36
69.7	0.8226	1.929	21.70	654.0		2.35
79.7	0.8143	1.868	20.81	630.8	$k_{(47.7-80.8)}=2.26$	2.34
93.8	0.8025	1.786	19.61	600.3		2.31
Mean = 2.32						2.36

i-Pitene (sample I). $M=136$. $r=0.02790$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.	$k_{(32.6-t)}$.
32.6	0.8513	2.124	24.73	728.1	$k_{(32.6-77.8)}=2.38$
35.6	0.8488	2.105	24.43	720.5	—
49.2	0.8377	2.019	23.13	688.2	$k_{(35.6-58.0)}=2.32$
61.4	0.8275	1.941	21.96	653.9	2.40
63.2	0.8260	1.930	21.80	655.1	$k_{(49.2-58.0)}=2.36$
77.8	0.8139	1.837	20.45	620.4	2.39
88.0	0.8054	1.775	19.60	598.9	2.36
93.8	0.8003	1.738	19.00	582.9	$k_{(61.4-85.0)}=2.33$
15.0	0.7994	1.731	18.91	580.5	2.37
				Mean = 2.35	2.38

i-Pinene (sample II). $M=136$. $r=0.04823$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.	$k_{(8.6-t)}$.
8.6	0.8725	1.318	27.22	788.0	$k_{(8.6-42.2)}=2.34$
9.3	0.8719	1.317	27.17	787.2	—
11.7	0.8699	1.307	26.86	780.5	$k_{(9.3-39.5)}=2.36$
23.9	0.8598	1.264	25.64	752.1	[1.14]
42.2	0.8446	1.199	23.96	709.3	$k_{(11.7-73.0)}=2.33$
59.5	0.8305	1.137	22.34	668.6	2.35
73.0	0.8192	1.089	21.15	637.7	$k_{(23.9-88.2)}=2.30$
88.3	0.8073	1.037	19.82	604.1	2.33
				Mean = 2.33	2.35

Limonene.

d-*Limonene*.—Purified by repeated distillation under diminished pressure. Boiling point $135^{\circ}/240$ mm.; $[\alpha]_D^{25} 122.6^{\circ}$.

l-*Limonene*.—Purified in a similar manner. Boiling point $100^{\circ}/73$ mm.; $[\alpha]_D^{25} -105.4^{\circ}$.

i-*Limonene*.—(Dipentene). Sample I. Repeatedly distilled. Boiling point $176^{\circ}/760$ mm.

Sample II. By mixing *d*- and *l*-limonenes to produce an inactive liquid.

d-*Limonene*. $M=136$. $r=0.04823$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.	$k_{(10.9-t)}$.
10.9	0.8511	1.417	28.53	840.0	$k_{(10.9-58.4)}=2.35$
23.1	0.8413	1.372	27.31	810.1	—
34.2	0.8329	1.334	26.41	788.9	$k_{(23.1-70.7)}=2.31$
44.4	0.8247	1.297	25.31	761.0	2.19
58.4	0.8138	1.247	24.00	728.4	$k_{(34.2-85.6)}=2.39$
70.7	0.8044	1.203	22.90	700.2	2.36
85.6	0.7927	1.150	21.57	665.9	2.34
90.3	0.7892	1.133	21.16	655.2	$k_{(44.4-90.3)}=2.30$
				Mean = 2.34	2.33

l-*Limonene*. $M=136$. $r=0.04823$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.	$k_{(8.2-t)}$.
8.2	0.8600	1.400	28.48	832.7	$k_{(8.2-57.1)}=2.25$
23.2	0.8464	1.342	26.87	794.1	—
35.4	0.8368	1.300	25.73	766.2	$k_{(23.2-71.2)}=2.23$
45.1	0.8291	1.267	24.85	744.6	2.28
57.1	0.8197	1.226	23.78	718.0	$k_{(35.4-82.1)}=2.23$
71.2	0.8085	1.179	22.55	687.3	2.26
82.1	0.7999	1.140	21.56	662.0	$k_{(45.1-85.5)}=2.20$
95.5	0.7895	1.096	20.48	633.9	2.25
				Mean = 2.23	2.26

i-Limonene (sample I). $M=136$. $r=0.04823$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.	$k_{(10.8-37.1)}=2.30$	$k_{(10.8-37.1)}$
10.5	0.8668	1.366	28.00	814.7		—
22.8	0.8670	1.322	26.80	785.6		2.38
34.6	0.8475	1.282	25.12	759.1	$k_{(32.8-68.2)}=2.26$	2.31
45.1	0.8393	1.245	24.72	734.6		2.32
57.1	0.8296	1.204	23.63	707.8	$k_{(34.6-81.7)}=2.25$	2.30
69.9	0.8195	1.160	22.50	679.1		2.29
81.7	0.8100	1.120	21.46	653.1	$k_{(45.1-89.8)}=2.24$	2.27
93.8	0.8004	1.077	20.40	625.7		2.27
					Mean = 2.26	2.29

i-Limonene (sample II). $M=136$. $r=0.04823$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.	$k_{(10.8-37.2)}=2.33$	$k_{(10.8-37.2)}$
10.8	0.8538	1.397	28.22	829.1		—
24.2	0.8432	1.349	26.90	797.1		2.39
35.0	0.8348	1.311	25.89	772.3	$k_{(34.2-69.5)}=2.29$	2.35
46.6	0.8247	1.270	24.78	745.0		2.35
57.2	0.8174	1.233	23.84	721.1	$k_{(35.0-81.7)}=2.29$	2.33
69.6	0.8076	1.190	22.73	693.3		2.31
81.7	0.7981	1.147	21.65	665.6	$k_{(46.6-96.2)}=2.26$	2.31
96.2	0.7868	1.096	20.40	633.1		2.30
					Mean = 2.29	2.33

Dimethyl d-Tartrate.—Repeatedly fractionated under low pressure. The sample employed boiled at $158^{\circ}/13$ mm., melted at 42.4° , and had $[\alpha]_D^{25} - 9.2^{\circ}$ (5 per cent. solution in chloroform).

Dimethyl Racemate.—Purified by distillation under diminished pressure. Boiling point $169^{\circ}/20$ mm.; melting point, 89.5° .

Methyl d-Tartrate. $M=178$. $r=0.04823$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.	$k_{(82.0-106.0)}=2.04$	$k_{(82.0-106.0)}$
62.0	1.2903	1.278	39.02	1042.0		—
62.6	1.2896	1.276	38.94	1040.0		[3.33]
67.2	1.2850	1.267	38.52	1031.5	$k_{(62.6-124.0)}=1.98$	2.02
96.3	1.2545	1.204	35.72	972.0		2.04
100.0	1.2506	1.196	35.39	964.6	$k_{(97.2-136.0)}=1.99$	2.04
124.0	1.2255	1.146	33.23	918.2		2.00
126.0	1.2235	1.142	33.06	914.6	$k_{(96.3-135.1)}=1.96$	1.99
135.1	1.2140	1.122	32.22	896.0		2.00
					Mean = 1.99	2.015

Methyl Racemate. $M=178$. $r=0.04823$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.	$k_{(89.6-180.6)}=2.04$	$k_{(89.6-180.6)}$
89.6	1.2604	1.181	35.22	955.2		—
92.5	1.2575	1.174	34.93	948.6		[2.22]
103.6	1.2458	1.149	33.86	925.6	$k_{(92.5-137.4)}=2.93$	2.11
124.8	1.2237	1.103	31.93	883.0		2.05
150.6	1.1968	1.045	29.59	830.5	$k_{(103.6-139.0)}=2.01$	2.04
157.4	1.1897	1.030	28.99	817.0		2.04
159.0	1.1880	1.027	28.86	814.1	$k_{(124.8-159.2)}=2.03$	2.03
159.2	1.1878	1.026	28.83	813.3		2.04
					Mean = 2.03	2.05

A comparison of the mean values of k , which are tabulated separately for convenience of reference, obtained with each set of

liquids, shows that the active and the inactive modifications in each case have the same degree of molecular complexity, and, therefore, that the inactive modifications are not racemic compounds.

The last column in each table gives the values of k calculated from the molecular surface energies at the lowest temperature and each succeeding temperature. The mean value in the last column agrees with the mean value obtained at approximately equal intervals of temperature over the whole range. The values in brackets have not been taken into account, being calculated from temperature differences too small to give accurate results. The individual values of k in the last column decrease slightly and fairly uniformly with rise of temperature. This cannot be taken as evidence of racemate formation, because the change occurs both with the active and inactive modifications. Neither can it be due to association, because no evidence has ever been placed on record of association being accompanied by an absorption of heat. It must be attributed to some unknown factor which is operating both in the active and the inactive modifications of the substance.

The case of the methyl esters of active and inactive tartaric acids is interesting. Our values of k are 1.99 and 2.03 respectively, corresponding with association factors (α) of 1.10 and 1.07. In the paper already referred to, Gróh obtains the values 2.37 and 2.26 respectively, corresponding with $\alpha=0.85$ and 0.91. It is, presumably, in view of the latter value that he concludes that the inactive form is unimolecular and not racemic; but by comparison with the value (0.85) for the active ester he would apparently have been justified in indicating slight molecular complexity for the racemate. Our results point to an anomalous state, the tartrate ($\alpha=1.10$) being more associated than the racemate. From these figures it appears that racemates have no existence in the liquid state:

	k .	k' .
<i>d</i> -Pinene.....	2.36	2.37
<i>l</i> -Pinene.....	2.32	2.36
<i>i</i> -Pinene (sample I.).....	2.35	2.38
„ (sample II.)	2.33	2.35
<i>d</i> -Limonene	2.34	3.335
<i>l</i> -Limonene	2.23	2.25
<i>i</i> -Limonene (sample I.)	2.26	2.29
„ (sample II.)	2.29	2.33
Dimethyl- <i>d</i> -tartrate	1.99	2.015
Dimethyl racemate	2.03	2.05

In conclusion, we wish to express our thanks to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

EAST LONDON COLLEGE.

*LV.—The Interaction of Chlorine and Hydrogen. The
Influence of Mass.*

By DAVID LEONARD CHAPMAN and LEO KINGSLEY UNDERHILL.

WHEN the conditions are such that a chemical change in a system can take place only under the influence of light, the velocity of the change is known to be proportional to the light absorbed by the coloured constituents of the system in unit time, provided that the character of the light and the composition of the system be fixed. If the light be monochromatic and the composition of the system be variable, the velocity of chemical change will be given by the numerical value of an expression of the form:

$$k_n E_n f_n(c_1, c_2 \dots),$$

in which E_n is the light energy, of frequency n , absorbed in unit time, k_n is a number the value of which depends on the vibration frequency, and $f_n(c_1, c_2 \dots)$ is an unknown function of c_1, c_2 , etc., the concentration of the constituents of the mixture, and possibly also of n .* It is assumed that the function in question is independent of the vibration frequency of the light, the rate of chemical change in a system illuminated by composite light would be given by the expression:

$$f(c_1, c_2 \dots) \int k_n \frac{dE_n}{dn} dn,$$

the limits of the integral being the maximum and minimum values of the vibration frequencies of the composite light.

In order to determine experimentally the nature of the function f the value of the integral $\int k_n \frac{dE_n}{dn} dn$ must during the course of the experiment be determinable at any moment, or be constant. By preference it should be maintained constant.

Unfortunately, in several investigations that have been undertaken with the object of estimating the influence of mass on photochemical changes the energy integral was not maintained constant, nor was any attempt made to estimate and to introduce a correction for its variation during the course of the reaction. M. Wilderman's experiments (*Phil. Trans.*, 1902, 199, 337) on the interaction of carbon monoxide and chlorine, for example, were vitiated by this source of error. Mixtures of carbon monoxide and chlorine

* It is probable, but by no means certain, that f is independent of n . It has been invariably assumed that such is the case, although the published experimental evidence which supports the assumption is not entirely satisfactory.

enclosed in a vessel of 3.5 cm. diameter were exposed to light, and the rates of union of the gases, determined from readings of the variations in pressure, taken at stated intervals of time, the readings being continued until a considerable proportion of the chlorine originally present had disappeared. Under such conditions the light absorbed must have diminished considerably during the progress of the experiment, and the conclusion drawn by Wilderman from his uncorrected measurements, namely, that the chemical change in question is bimolecular, and conforms to the same law of mass as a purely idiochemical change, cannot therefore be accepted as valid. Strictly, his experiments can be taken only to indicate that, under conditions which would secure a constant rate of absorption of light, the order of the change would be lower than the second.

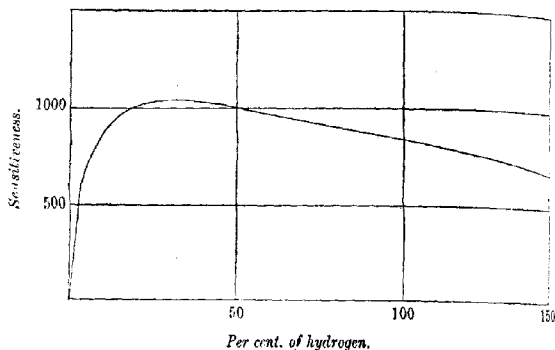
At first sight it might appear that the photochemical interaction of carbon monoxide and chlorine would be a particularly suitable change to investigate with the object of estimating the influence of mass on the velocity of a photochemical transformation; but in practice we have found that a serious obstacle is presented to its investigation owing to the difficulty of obtaining mixtures of the gases containing only such inhibitive impurities as are not slowly changed or destroyed by the influence of the light as the action proceeds. The impurities in question are contained in the carbon monoxide, and we have up to the present failed to effect their complete removal, in spite of numerous attempts by various methods. Accordingly we have had to fall back on the action between chlorine and hydrogen. Although the rate of interaction between these gases cannot be measured with such ease as that between chlorine and carbon monoxide, yet the mixture can, with the exception of oxygen (which does not alter in amount under the influence of light), be obtained uncontaminated with impurities which retard the change.

Our object has been to investigate, in the first place, the influence of the concentration of the hydrogen on the rate of formation of hydrogen chloride. The partial pressures of the chlorine and of the oxygen in the mixtures examined in one series of experiments were therefore kept constant, whereas that of the hydrogen was varied. A small amount of oxygen was added to the chlorine in order to make it quite certain that the mixtures rich in hydrogen did not contain an appreciably larger proportion of oxygen than those poorer in hydrogen, as would otherwise have been the case if the hydrogen had adventitiously, or as a result of its method of preparation, contained a trace of oxygen. The intensity of illumination was always the same, and, as the concentration of the

chlorine was also invariable, the energy absorbed by the different mixtures in unit time was constant.

It was found that as the partial pressure of the hydrogen was increased from zero the rate of formation of hydrogen chloride was at first almost proportional to the partial pressure of the hydrogen; but the ratio of partial pressure of hydrogen to velocity of interaction rose continuously in value as the proportion of hydrogen was increased, and when the pressure of hydrogen had attained a definite value the rate of formation of hydrogen chloride became a

FIG. 1.



maximum. Then, as the proportion of hydrogen was still further increased, the rate of interaction of the chlorine and hydrogen fell very slowly. If the percentage of hydrogen is plotted against the sensitiveness, a curve of the form shown in Fig. 1 is obtained.

Results of the character just indicated were not unexpected, and, indeed, they admit of a simple explanation with the aid of the theory of photochemical change formulated in previous papers. They appear, however, to be at variance with views recently expressed by Weigert (*Ann. Physik*, 1907, [iv], **24**, 155 and 243) on the nature of photochemical changes of the class under consideration. It is desirable that the bearing of our results on these views should be briefly considered.

Weigert, from certain observations made while he was investigating the interaction of chlorine and carbon monoxide, arrived at the conclusion that the action of light is catalytic, or more precisely that the light generates nuclei, in the vicinity of which the latent or almost latent forces of affinity become abnormally active and are

thus rendered capable of impelling the system into the most stable state of chemical composition. If this is a complete account of the mechanism of the photochemical interaction of chlorine and carbon monoxide, and of chlorine and hydrogen, the conclusion that the rate of the action ought to be proportional to the colourless constituent of the mixture appears to be almost inevitable. This consequence of the theory, however, is obviously not in harmony with the results of our experiments, according to which the rate of interaction of the gases is nearly independent of the proportion of hydrogen when the latter exceeds a definite value. The result on which Weigert bases his theory appears to us to be a consequence of the thermodynamic principles, and therefore consistent with any mechanical hypothesis which does not contradict those principles.*

The theory about to be advanced is of limited application, in so far as it is capable at present of being verified by quantitative relations; but it will be convenient to postpone the defining of these limitations until a general outline of the theory has been presented.

The photochemical transformation of chlorine and hydrogen into hydrogen chloride is accompanied by a fall in free energy vastly greater than the light energy required to induce the change. An hypothesis capable of giving a satisfactory mechanical account of the fact that the free energy of the system cannot, without the assistance of a relatively small supply of highly efficient external energy, break up the molecules of the elements and bring into operation the force of affinity between the atoms of chlorine and hydrogen, is not likely to be discovered until a much more intimate knowledge of the internal structure of the atoms has been gained; but it is probable, we believe, that such an hypothesis might not unprofitably be sought for in the periods of free vibration of the valency electrons. We are, however, at present only concerned with the correlation of the small but necessary supply of external energy and the extent of the chemical change induced by it.

Consider the effect of exposing to light a mixture of chlorine, hydrogen, and a relatively small amount of oxygen. The light is absorbed by the chlorine, and exists for a time in the molecules of that substance as a form of energy of vibration which is incapable without further modification of promoting the union of the

* In support of his conclusions, Weigert quotes the results of Bevan (*Phil. Trans.*, 1903, A, 202, 71) on cloud formation in a moist illuminated mixture of chlorine and hydrogen. For comments on Bevan's conclusion, the reader is referred to the paper on the interaction of chlorine and hydrogen by Burgess and Chapman.

hydrogen and chlorine. Of this vibrational energy by far the larger part is degraded, and thereby rendered ineffective by the agency of the oxygen, the proportion thus dissipated depending almost entirely on the partial pressures of the chlorine and oxygen, and being therefore almost the same when the concentration of both of these gases is kept constant. The vibrational energy which escapes dissipation by this process is transformed into a comparatively stable and still highly efficient form, and as such is accumulated in the chlorine molecules, which are thereby rendered abnormally active. The latter form of energy which endows the chlorine molecules with chemical activity we shall for brevity call the actinic energy. If the mixture contains no hydrogen the actinic energy is dissipated, the rate of dissipation being for the same concentration of chlorine proportional to its amount in unit volume. If the mixture contains hydrogen, however, a part only of the actinic energy will be directly dissipated, the rest being utilised and degraded in the promotion of chemical change (the proportion of actinic energy lost by direct dissipation being almost zero when the concentration of the hydrogen is high).

We shall now show that the quantitative results are in accordance with the above view of the mechanism of the change. To this end we shall deduce from the theory what ought to occur in an element of volume of a system composed of chlorine, hydrogen, and oxygen under the influence of light. Let U be the light energy absorbed in unit volume by the chlorine in unit time, and let V be the vibrational energy in unit volume. The vibrational energy supplied in unit time by the light is obviously U , whilst that lost in unit time by dissipation is given by CV , C being a function of the concentration of the chlorine and oxygen. In the steady state the gain and loss of V must be equal, or $V=U/C$. The actinic energy acquired by the chlorine in unit time is proportional to V , and since $V=U/C$ it must be given by kU , k being a function of the concentration of the oxygen and chlorine. The actinic energy in unit volume being denoted by X , the amount dissipated in unit time is obviously proportional to X , and may therefore be put equal to cX (c being a constant), whilst that which is degraded in bringing about the union of the chlorine and hydrogen is given by $K[\text{H}_2]X$, in which K is a constant, and $[\text{H}_2]$ the concentration of the hydrogen.

Accordingly, $dX/dt = kU - cX - K[\text{H}_2]X$.

But in the steady state which is attained in an immeasurably short period of time after the commencement of the illumination $dX/dt = 0$.

$$\therefore kU = cX + K[\text{H}_2]X.$$

The last term on the right hand side of the equation is equal to the actinic energy employed in unit time in converting chlorine and hydrogen into hydrogen chloride, and the rate of formation of hydrogen chloride may be taken as proportional to the magnitude of the same term, if we may assume—the justification for the assumption cannot be conveniently given until later—that for photochemical changes of the class to which the interaction of chlorine and hydrogen belong, the hydrogen chloride formed is proportional to the actinic energy required for its production.

When the concentration of the hydrogen is small, $kU = cX$, and therefore $X = kU/c$.

Accordingly, the rate of formation of hydrogen chloride is approximately proportional to:

$$kKU/c[H_2].$$

Now kKU/c is constant when the concentrations of the chlorine and oxygen, and the intensity of illumination, are kept constant—as they were in one series of our experiments—and, therefore, under such conditions the rate of formation of hydrogen chloride ought to be proportional to $[H_2]$ when $[H_2]$ is small.

When the concentration of the hydrogen is relatively large,

$$kU = K[H_2]X,$$

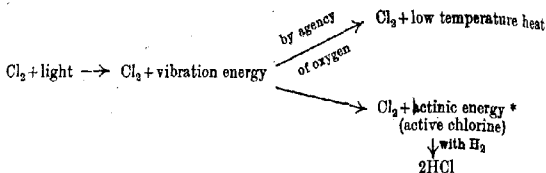
the interpretation of which is that the rate of formation of hydrogen chloride ought to be approximately constant, when the light absorbed and the partial pressures of the chlorine and oxygen are kept constant as they were in a series of our experiments.

It will be seen that the experimental results are in general agreement with the requirements of the theory. It only remains to account for the gradual fall in the rate of interaction of the chlorine and hydrogen when the pressure of the hydrogen is increased from a given limiting value. We believe that this fall is due to the circumstance that hydrogen, like oxygen, is capable, although in a very limited degree, of degrading the vibrational energy from which the actinic energy is derived.*

The transformations conceived to take place in the energy associated with the chlorine molecules, and the subsequent formation of hydrogen chloride, can be conveniently summarised with the aid of the following scheme:

* The fact that hydrogen diminishes, in a relatively slight degree, the phosphorescence of iodine vapour can be advanced in support of this view.

In the expressions developed above, the effect of the slight degradation of vibrational energy by hydrogen has been left out of account.



It is probable that the vibrational energy is composite, and that its character depends on the nature of the stimulating light. This question is at present under investigation.

At first sight it may not be obvious why it has been assumed that the chlorine can be associated with two distinct kinds of efficient energy designated respectively the vibrational energy and the actinic energy, the latter (to which the union of the chlorine and hydrogen is due) being derived from the former (which is degradable by oxygen, but incapable of effecting the union of the chlorine and hydrogen). The reason is that if the chlorine were associated with one kind of energy only—the vibrational energy—(which must be supposed to be both degradable by oxygen and effective in bringing about the union of chlorine and hydrogen), then clearly the rate of formation of hydrogen chloride ought continuously to approach a maximum value independent of the concentration of the oxygen as the relative proportion of impacts of chlorine molecules with oxygen and hydrogen molecules respectively is diminished, that is, as the concentration of the hydrogen is increased, that of the oxygen being constant. Whereas, of course, the maximum sensitiveness attained increases rapidly as the oxygen is diminished.

An alternative hypothesis, which is probably no more than a special case of the foregoing, is the following. The fraction of the vibrational energy which is not dissipated by the agency of the oxygen converts some of the chlorine into a very unstable and active allotropic modification, which is capable of reacting with hydrogen. If a sufficient number of hydrogen molecules are present in unit volume of the mixture practically every active chlorine molecule generated by the influence of the light makes a fruitful impact with a hydrogen molecule, and since the number of active chlorine molecules produced is proportional to the light absorbed, the hydrogen chloride formed under these conditions will also be proportional to the light absorbed. If, however, the hydrogen

* It is possible that Strutt's active form of nitrogen consists of ordinary molecules of nitrogen rendered active in the same way as we conceive that chlorine molecules are rendered by the agency of light.

molecules are scarce, most of the active chlorine molecules will, on account of their extreme instability, revert to inactive molecules, and only a small number of them will make fruitful impacts, the percentage of active molecules which make fruitful impacts being proportional to the concentration of hydrogen.

It is now desirable that we should examine a little more closely the energetics of the hydrogen-chlorine reaction. We shall, thereby, be enabled to offer further justification for our main assumption, namely, that the quantity of actinic energy and the amount of chemical change induced by it are equivalent, or, in other words, that the decrease in X attributable solely to the formation of hydrogen chloride is proportional to the hydrogen chloride produced. We shall be enabled also to define the class of chemical change to which the same assumption may be legitimately applied.

It is a simple matter to show that the fall in free energy during the formation of two gram-molecules of hydrogen chloride is given by the expression:

$$Rt \left(\log_e \frac{[\text{HCl}]^2}{[\text{H}_2][\text{Cl}_2]} - \log_e \frac{[\text{HCl}]^2}{[\text{H}_2][\text{Cl}_2]} \right),$$

in which a symbol enclosed in square brackets signifies the concentration of the gas corresponding with the symbol, and a square bracket with a dash indicates a concentration in a system in equilibrium.

If $[\text{HCl}]'$ is made equal to $[\text{HCl}]$, the expression reduces to:

$$Rt \log_e \frac{[\text{H}_2][\text{Cl}_2]}{[\text{H}_2][\text{Cl}_2]}.$$

Now in ordinary circumstances the product $[\text{H}_2][\text{Cl}_2]'$ is extremely small in comparison with $[\text{H}_2][\text{Cl}_2]$, and therefore the numerical value of the above expression is large, and will be very little affected by very appreciable alterations in either $[\text{H}_2]$ or $[\text{Cl}_2]$.

Accordingly, the efficient energy in the system itself available for the purpose of converting the chlorine and hydrogen into hydrogen chloride is almost constant, that is, is almost independent of the pressure of the hydrogen or chlorine. In other words, the tendency of the chlorine and hydrogen to change into hydrogen chloride is almost independent of the partial pressure of the former gases; and, therefore, if in addition to the energy of the system a small quantity of energy of greater efficiency than that contained in the system is required to bring about a definite amount of chemical change, the quantity of additional energy will be constant, it being assumed, of course, that its quality is the same. Our principal assumption could not be made for a system near the condition of equilibrium, since in that case a small variation in the concen-

tration of one of the interacting constituents would appreciably alter the tendency of the change to take place in a given direction, and therefore the additional supply of actinic energy required to bring about a stated amount of chemical change would not be independent of the constitution of the system.

It will consequently be perceived that without modification the above theory can only apply to photochemical changes of the same class as that under consideration, namely, to those changes which are attended by a considerable fall of chemical potential. It is, we believe, impossible to elaborate a satisfactory quantitative theory of the dynamics of photochemistry applicable to every class of chemical change without the assistance of much more experimental information than is at present available for the purpose.

EXPERIMENTAL.

The chlorine and hydrogen were prepared by the electrolysis of concentrated hydrochloric acid. In the preparation of the hydrochloric acid the greatest care was taken to prevent contamination with organic impurities, as these would have furnished inhibitors which could only have been removed from the interacting gases with extreme difficulty, and trustworthy actinometric measurements cannot, of course, be made so long as the chlorine and hydrogen contain the least trace of inhibitive impurity. Into chlorine-water which had been boiled for many hours hydrogen chloride was passed until the liquid was saturated. The hydrogen chloride was prepared by the action of concentrated sulphuric acid on common salt. The common salt was prepared in the usual way by its precipitation from a solution of brine with hydrogen chloride. In order to destroy organic impurities in the concentrated sulphuric acid, the latter was first heated with chlorine, and then, after sodium peroxide has been dissolved in it, boiled until the resulting persulphuric acid had been destroyed. The apparatus employed to electrolyse the hydrochloric acid has already been described (Chapman and MacMahon, T., 1909, 95, 135).

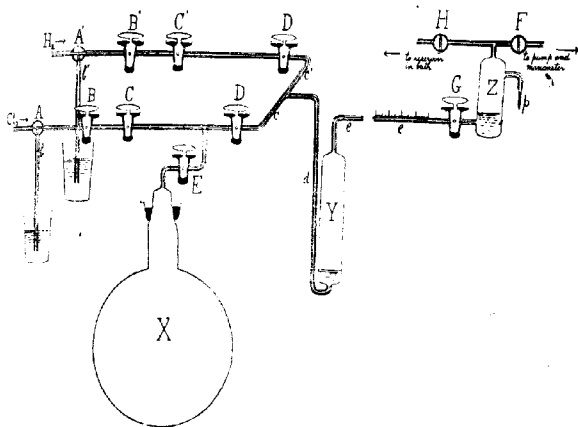
A diagrammatic representation of the essential part of the apparatus is given in Fig. 2.

X is a large globe which is used to contain the mixture of chlorine and oxygen. *Y* is the insulation vessel of the actinometer which is immersed in a large glass tank filled with water, the water being kept at a constant temperature of 20° with the aid of an electric thermo-regulator. The index tube *e* of the actinometer communicates through the tap *G* with the reservoir *Z*. By opening the tap *F* the reservoir can be brought into communication with a

water-pump and a manometer, neither of which are shown in the diagram. The reservoir is also in connexion with a large glass bottle immersed in the same tank as the actinometer, the pressure above the liquid in *Z* being thereby maintained constant.

The filling of the globe *X* was accomplished in the following way: The hydrochloric acid was electrolysed, and the chlorine and hydrogen permitted to escape through the tubes *b* and *b'* until all the air had been expelled from the cell and delivery tubes. In the meanwhile, before water had been introduced into *Y* and *Z*, the apparatus, including the globe, from the taps *B*, *B'*, and *H* to

FIG. 2



the pump was exhausted. After closing *H*, the tap *B* was very cautiously turned just sufficiently to admit chlorine to the exhausted apparatus at such a rate that the gas did not cease to enter slowly the potassium hydroxide solution under *b*. When the pressure in the globe had risen to about 15 cm. of mercury, the apparatus was again exhausted. The operation of filling with chlorine to 15 cm. and exhausting was repeated four times. The taps *D* and *D'* were then closed, and the globe *X* completely filled with chlorine, an operation which took about six hours. The pressure in the globe was then reduced below the atmospheric pressure to an extent depending on the amount of oxygen it was desired to introduce into the globe. After the tap *E* had been closed, the potassium hydroxide solution removed from under *b*, the electrolysis of the hydrochloric acid in the cell discontinued, and the three-way tap *A* turned so that *b* communicated with the apparatus and not with

the cell, a slow stream of oxygen was passed through *b* in the direction *A, B, C, D*, etc., until the chlorine had been removed from the capillary tubes. The tap *E* was next opened, and the oxygen permitted to enter the globe until the pressure was again that of an atmosphere. Then the tap *E* was closed, and the oxygen and chlorine in the globe allowed to mix, a process for the completion of which it was found desirable to assign at least two days. Water which had been previously digested for many hours with chlorine was introduced into the reservoir *Z* through the side-tube *p*, which was drawn out to a capillary tube to permit of its being easily opened and closed by respectively breaking off the tip with the aid of a file, and fusing up the open end before the blow-pipe. Of the water thus introduced into *Z* a convenient quantity was admitted into the insolation vessel through the tap *G*, the pressure in the insolation vessel having been previously reduced below that in *Z*. The filling of the insolation vessel with a mixture of known composition of hydrogen and of the gas contained in the globe was accomplished in a similar manner to the filling of the globe. With *B, B'*, and *E* closed, and the other taps open, the apparatus was exhausted. Hydrogen was then admitted to the apparatus through *B'*, and pumped out again several times until all oxygen had been removed from the actinometer and delivery tubes. Then with the tap *D'* closed the insolation vessel *Y* was washed out several times with the gas in *X*, and then filled with the same gas. By gently shaking *Y* the water which it contained was saturated with chlorine. The pressure in *Y* was then reduced to 30 cm. of mercury, the precaution being, of course, taken to remove the excess of chlorine from the liquid. Hydrogen was then admitted to *Y* until its partial pressure had reached the desired value. This operation demanded the exercise of some care; it was accomplished by adjusting the pressure in *Z* to the required value, allowance being made for the liquid contained in the vessel, then admitting hydrogen into the insolation vessel very slowly with the tap *G* partly turned on, so that the liquid in the index *c* could only move slowly in the direction of lower pressure, and when the forward movement of the index liquid had ceased, turning the tap *G* full on, the hydrogen being shut off as soon as the index liquid had reached the zero point on the scale.

The insolation vessel of the actinometer was illuminated with a Hefner lamp. The position of the lamp was unaltered during a series of observations; but in order to secure a convenient rate of formation of hydrogen chloride the intensity of illumination was altered from series to series, being greater for mixtures which contained a larger amount of oxygen. When the mixture is exposed

to light great care must be taken that the index has come to its position of equilibrium before taking the initial and final readings of its position. Attention to this precaution is particularly necessary after the mixture has been exposed to light, as the index recedes slowly for several hours after hydrogen chloride has been formed in the insolation vessel. This apparent expansion of the gas in the actinometer after exposure to light has been found to be due to the formation of a supersaturated solution of chlorine in the liquid enclosed in the insolation vessel, and to this solution slowly giving up its excess of chlorine. The excess of chlorine passes out of solution more rapidly, of course, if the actinometer is gently shaken. The cause of the formation of a supersaturated solution of chlorine is fairly obvious. The hydrogen chloride generated by the action of the light dissolves in the surface layer of water, and in the concentrated hydrochloric acid produced the chlorine is extremely soluble. The solution of chlorine in concentrated hydrochloric acid is, however, rapidly diluted by the process of diffusion, and the chlorine being less soluble in dilute hydrochloric acid tends to escape. The relative amount of hydrochloric acid produced in unit time is obtained by dividing the product of the total movement of the index and the pressure of the gas in the actinometer by the time of exposure. The results are tabulated below:

Series.	Pressure of hydrogen Pressure of chlorine.	Pressure of oxygen in cm. of mercury.	Sensitiveness.
I.	0.485	very small	1000
	0.894	" "	786
II.	0.511	0.25	1000
	1.000	0.25	682
	1.472	0.25	636
	0.0235	0.25	489
III.	0.510	0.60	1000
	1.020	0.60	734
	1.469	0.60	689
	0.0318	0.60	431
IV.	0.510	0.60	1000
	1.536	0.60	688
V.	0.521	1.20	1000
	1.579	1.20	637

It will be observed from the above table that a mixture which contains equal volumes of chlorine and hydrogen is not twice as sensitive as one which contains only 3 per cent. of the latter gas.

The pressure of the chlorine was nearly 30 cm. in all the experiments. For the purpose of comparison the sensitiveness of each mixture is compared with that of the mixture in the same series which contained two volumes of chlorine to one of hydrogen. The

numbers given for the sensitiveness are the means of several determinations in most cases.

The fall in sensitiveness resulting from an increase in the proportion of hydrogen present appears to be less marked as the pressure of oxygen is increased.

It will be observed that a mixture which contains equal volumes of chlorine and hydrogen is never the most sensitive, the maximum sensitiveness being given by a mixture containing a considerably lower proportion of hydrogen.

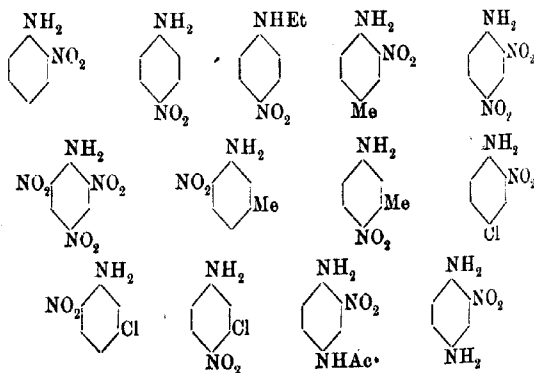
SIR LEOLINE JENKINS LABORATORY,
JESUS COLLEGE, OXFORD.

LVI.—*Quinonoid Salts of Nitroanilines.*

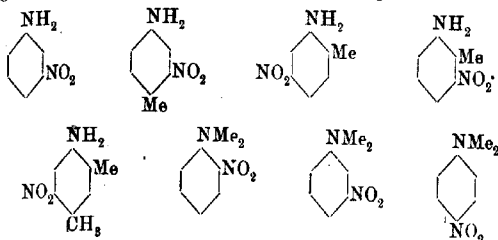
By ARTHUR GEORGE GREEN and FREDERICK MAURICE ROWE.

IN a previous communication (T., 1912, 101, 2452) indirect evidence has been adduced in favour of the view that in alkaline solutions the orthonitroamines of the benzene series exist (in part at least) in the form of salts of the quinonoid type, $R \begin{smallmatrix} \text{NH} \\ \text{NO}_2 \end{smallmatrix} M$.

With the object of isolating such salts in an analysable form and of investigating their conditions of formation, we have examined the behaviour of a number of nitroamines, ortho, meta, and para, on treatment in benzene solution with sodium ethoxide. The following nitroamines gave under these conditions deep orange to red precipitates of the sodium salts insoluble in benzene:



On the other hand, no precipitates were obtained, and no change of colour was observed with the following:

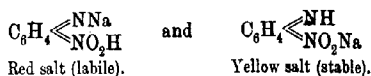


It would therefore appear that all primary and secondary ortho- and para-nitroamines give rise to deeply-coloured salts under the conditions employed, but that no such quinonoid change occurs in the meta-series. It is also apparent from the behaviour of the *o*- and *p*-nitrodimethylanilines that no salts are obtainable when both hydrogen atoms of the amino-group are replaced by alkyl groups. The absence of reaction in the meta-series is noteworthy in view of the still open question of the existence of meta-quinonoid compounds (compare Hantzsch, *Ber.*, 1906, **39**, 1096; Meyer and Desamari, *Ber.*, 1908, **41**, 2437; Stark and Garben, *Ber.*, 1913, **46**, 659).

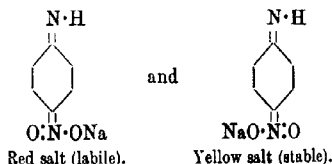
The quinonoid salts of the ortho- and para-nitroamines are very unstable substances, becoming rapidly decolorised on exposure to damp air. In order to obtain the compounds in an analysable form it is necessary to work rapidly, and to carefully exclude all moisture by the use of solvents dried over sodium. The precipitates were collected quickly on a Büchner funnel, washed with hot dry benzene, followed by anhydrous ether, and finally dried in a vacuum desiccator over sulphuric acid. They form deep yellow, orange, or red powders insoluble in benzene. In the dry state they can be kept unchanged, but on treatment with water they are hydrolysed at once, giving the parent nitroamine, and leaving free alkali hydroxide in solution. On this fact was based a method for their analysis. A weighed quantity of the dry salt was treated with water, and the precipitated nitroamine separated and washed free from alkali. The filtrate and washings were then titrated with standard sulphuric acid, employing methyl-orange as indicator. In every case the results correspond closely with those required for a monosodium or monopotassium salt of the quinonoid nitronic acid, $R \begin{smallmatrix} \text{NH} \\ \text{NO}_2 \end{smallmatrix} \text{H}$. The possibility of these salts having a quinonitronic acid constitution, $\begin{smallmatrix} \text{EtO} \\ \text{NH}_2 \end{smallmatrix} > R : \text{NO}_2 \text{M}'$, analogous to that which has

been assigned to the coloured salts derived from *s*-trinitrobenzene and from picrylaniline (compare Busch and Kögel, *Ber.*, 1910, 43, 1549), is excluded by the absence of ethyl groups (negative result with Zeisel test). It was further ascertained by blank experiments that under the conditions employed no concomitant precipitation of sodium ethoxide can occur.

In the case of *p*-nitroaniline two differently coloured sodium salts were obtained, a yellow and a red, according to the conditions employed. The red salt is fairly stable in the presence of an excess of *p*-nitroaniline, but as soon as a quantity of sodium ethoxide is added sufficient to produce alkalinity of the benzene solution (dry phenolphthalein paper as indicator) it changes suddenly into the yellow and more stable form. When *p*-nitroaniline is replaced by its monoethyl derivative only one salt was obtainable, and this appeared to correspond with the yellow form. This observation seems to lend some support to the possibility that the two salts of *p*-nitroaniline may be constitutionally isomeric in the sense of the formulæ:



On the other hand, in view of the fact that we failed to obtain a disodium salt of *p*-nitroaniline, $\text{C}_6\text{H}_4 \begin{array}{c} \text{NNa} \\ \text{NO}_2\text{Na} \end{array}$, by employing a large excess of sodium ethoxide, and that similar pairs of coloured isomerides have been met with by Hantzsch in the case of the nitrophenol salts and by Sudborough and Picton (*T.*, 1906, 89, 586) in the case of free picrylarylamines (see also Hantzsch, *Ber.*, 1910, 43, 1651, 1662), it appears more probable that the isomerism is of the kind termed by Hantzsch "chromoisomerism," and is possibly produced by differences in steric configuration; thus the two salts in question might be represented by the formulæ:



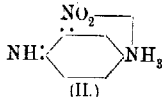
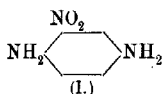
It may be noted that under the conditions in which all the quinonoid salts were prepared (benzene or toluene containing a little alcohol) these salts undergo a certain degree of dissociation. This is least at the boiling point of the solvent, but increases rapidly as the temperature is lowered, until in a freezing mixture the precipitate (in the case of *o*- and *p*-nitroaniline) disappears

completely, leaving a pale yellow solution of the free nitroaniline. On heating this cooled solution the precipitation of the coloured sodium salt recommences, and is again almost complete at the boiling point. The equilibrium of the system:



is therefore determined to the right by high temperatures, to the left by low.

The tendency of nitroamines to give quinonoid salts is further exemplified by the behaviour of nitro-*p*-phenylenediamine. This compound crystallises from water in magenta-red needles, having a dark green reflex. In water and in alcohol it dissolves (0.1 per cent. solutions) with a deep blood-red colour, and from the aqueous solution wool is dyed nearly the same shade. On the other hand, the solutions of the substance in benzene, toluene, or xylene (0.1 per cent. solutions) are yellow, those in chloroform and ether a rather redder yellow, and those in acetone and nitrobenzene an orange tint intermediate between the colour of the alcoholic and benzene solutions. The monohydrochloride of the base is bright yellow. These facts point to the conclusion that whilst the ordinary formula (I) correctly represents the constitution of the base in hydrocarbon solvents, the solid substance is actually an internal



quinonoid salt of the formula (II), which in the main is also the condition of the compound in its aqueous and alcoholic solutions and when dyed on animal fibres. In solvents of intermediate ionising power a mixture of the two forms is present. The addition of sodium ethoxide to the yellow benzene solution causes the precipitation of a dark red sodium salt of very similar colour to that of the free compound in the solid state.

EXPERIMENTAL.

Sodium Salt of o-Nitroaniline.

It was found advisable in this case to employ the nitroamine in excess. Twenty-five c.c. of a benzene solution of sodium ethoxide, obtained by dissolving 1 gram of sodium in 15 c.c. of absolute alcohol, and diluting with dry benzene to 100 c.c., were added to a boiling solution of 2 grams of *o*-nitroaniline in 120 c.c. of dry toluene. The brownish-red precipitate was collected while hot, washed, and dried as already described. It forms a reddish-brown

powder, which on contact with water yields *o*-nitroaniline. Titration with sulphuric acid gave $\text{Na}=14.31$ (mean). $\text{C}_6\text{H}_5\text{O}_2\text{N}_2\text{Na}$ requires $\text{Na}=14.37$ per cent.

Sodium Salt of p-Nitroaniline (Red Form).

Fifty c.c. of a benzene solution of sodium ethoxide, obtained as above, were added quickly to a hot solution of 6 grams of *p*-nitroaniline in 450 c.c. of dry toluene. The orange-red precipitate was collected at once, and boiled with 150 c.c. of dry toluene to remove excess of *p*-nitroaniline. The precipitate was again collected, and washed with boiling toluene, followed by anhydrous ether. The dry salt is orange-red. Titration with sulphuric acid gave $\text{Na}=14.28$ (mean). $\text{C}_6\text{H}_5\text{O}_2\text{N}_2\text{Na}$ requires $\text{Na}=14.37$ per cent.

Sodium Salt of p-Nitroaniline (Yellow Form).

Thirty c.c. of the same benzene solution of sodium ethoxide were added to a boiling solution of 2 grams of *p*-nitroaniline in 150 c.c. of dry benzene. The yellow precipitate was collected and washed with benzene and ether. By treatment with water *p*-nitroaniline is regenerated.

Found: $\text{Na}=14.22$ (mean).

$\text{C}_6\text{H}_5\text{O}_2\text{N}_2\text{Na}$ requires $\text{Na}=14.37$ per cent.

Sodium Salt of p-Nitroethylaniline.

Thirteen c.c. of a solution of sodium ethoxide obtained by dissolving 1 gram of sodium in 15 c.c. of absolute alcohol and diluting with dry benzene to 50 c.c. (that is, double the strength of that used before) were added to a solution of 2 grams of *p*-nitroethylaniline in 50 c.c. of dry toluene. The precipitate, although orange-yellow at first, rapidly darkens in colour, and appears to undergo a certain amount of decomposition.

Found: $\text{Na}=12.28$ (mean).

$\text{C}_8\text{H}_9\text{O}_2\text{N}_2\text{Na}$ requires $\text{Na}=12.23$ per cent.

Sodium Salt of m-Nitro-p-toluidine, ($\text{CH}_3:\text{NH}_2:\text{NO}_2=1:4:3$).

This was prepared in the same manner as the sodium salt of *o*-nitroaniline. It forms a reddish-brown powder of redder shade than the *o*-nitroaniline salt.

Found: $\text{Na}=13.28$.

$\text{C}_7\text{H}_7\text{O}_2\text{N}_2\text{Na}$ requires $\text{Na}=13.22$ per cent.

Potassium Salt of 2:4-Dinitroaniline.

Twenty c.c. of a solution of alcoholic potassium hydroxide obtained by dissolving 1 gram of potassium hydroxide in 30 c.c. of absolute alcohol were added to 2 grams of dinitroaniline dissolved in 250 c.c. of dry benzene. The purplish-crimson precipitate which separated was collected, washed, and dried as before. The dry salt forms a purplish powder. It readily deflagrates on heating. On treatment with water dinitroaniline was regenerated.

Found: $K=17.33$ (mean).

$C_6H_3O_4N_2K$ requires $K=17.65$ per cent.

The sodium salt, prepared by employing sodium ethoxide, is similar in appearance and properties.

Potassium Salt of 2:4:6-Trinitroaniline (Picramide).

This was prepared in the same manner as the preceding. The dry salt has a reddish-brown colour, and explodes violently on heating to about 110° .

Found: $K=14.53$ (mean).

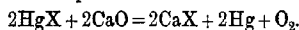
$C_6H_2O_6N_3K$ requires $K=14.66$ per cent.

DEPARTMENT OF TINCTORIAL CHEMISTRY,
THE UNIVERSITY, LEEDS.

LVII.—*The Estimation of Mercury as Metal by the Dry Method.*

By ALEXANDER CHARLES CUMMING and JOHN MACLEOD.

MERCURY compounds, when heated with calcium oxide, are decomposed according to the equation:



Nearly seventy years ago Erdmann and Marchand (*J. pr. Chem.*, 1844, **31**, 385) applied this reaction to the determination of the atomic weight of mercury. Their method has since been used for the estimation of mercury (König, *J. pr. Chem.*, 1857, **70**, 64). Treadwell ("Analytical Chemistry," English edition, 1908, **2**, 136) recommends this method as giving exact results, but states that it is nevertheless preferable, when possible, to precipitate as sulphide.

Many modifications have been proposed at different times, and there is general agreement that results of a high degree of accuracy are attainable, but that the method is troublesome. The original method could not be used for mercuric iodide, but Rose (*Ann. Phys.*

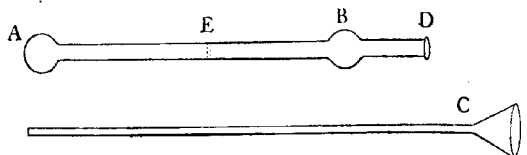
Chem., 1860, [ii], 110, 542) found that accurate results were obtained if finely divided copper was added to the mixture ^{were} of mercury salt and lime.

The special advantage of the dry method is that it is applicable to ores and minerals without previous removal of any other metals. The disadvantage is, as we have already indicated, the experimental difficulty; we believe that this has been largely overcome by the use of the apparatus and by the procedure described below.

EXPERIMENTAL.

The apparatus used by Penfield (*Amer. J. Sci.*, 1894, [iii], 48, 31) for the determination of water in minerals was found suitable for our purpose. A piece of glass tubing about 20 cm. in length

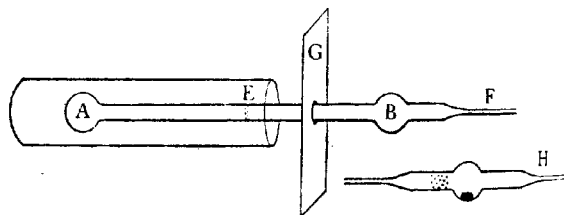
FIG. 1.



and 5 mm. in diameter was closed at one end, and small bulbs blown at *A* and *B* (Fig. 1).

The tube was cleaned, dried, and weighed. By means of the long funnel, *C*, a suitable quantity of the substance to be analysed was introduced into the bulb *A*, and the tube and contents weighed.

FIG. 2.



A mixture of iron filings and quicklime was then added by means of the funnel *C*, from which any adhering traces of the substance had meanwhile been removed. The mixture introduced into the

bulb *A* consisted mainly of iron filings, which were well mixed with the substance by rotating the tube. A mixture of about equal parts of iron filings and quicklime was then added until about 8 cm. of the tube had been filled. A small plug of asbestos, *E*, was introduced, so that, after tapping the tube, only a very shallow air-channel remained along the top. The open end, *D*, was then drawn out into a fine capillary, as in *F*, Fig. 2.

The prepared tube was placed in an iron tube which could be heated by a flat-flamed burner. (We used a piece of iron gas-pipe about 15 cm. by 1.5 cm., and closed the ends with plugs of asbestos fibre.) The bulb *A* was wrapped in some asbestos paper to prevent it coming into direct contact with the iron tube, and thereby being heated before the narrow part of the tube; if this precaution was omitted, the mercuric salt was partly volatilised without decomposition.

An asbestos shield, *G*, prevented the heat from reaching the bulb *B*, which was cooled by wet filter paper.

The iron tube was heated, at first with a small flame and at the end nearer *G* only. The heating was gradually increased, and the flame moved backwards until the whole iron tube was heated to a low red heat. The apparatus was almost horizontal, but the end *F* was slightly lower than the closed end, so that, on gently tapping the tube, any mercury which had condensed beyond the asbestos screen formed a globule and ran into the bulb *B*. When all the mercury had distilled (usually after one hour) the glass tube was drawn out until the plug *E* was exposed. At the same time the burner was drawn forward, so that the flame played directly on the glass tube. As soon as the glass tube became red hot it was drawn off about midway between the plug *E* and the bulb *B*. The mercury was thus obtained in a tube, as shown at *H* in Fig. 2.

It was observed that if the remainder of the original tube was left with only a small portion projecting from the hot furnace, any residual mercury collected in the exposed cooler portion of the tube. By examination with a lens very small quantities of mercury could be detected in this way, and a useful check on the analysis was thereby obtained.

To remove water, a current of dry air was drawn through the tube until the weight was constant. The main portion of the mercury was then shaken out of the tube, and the portion adhering to the glass removed by blowing air through the gently heated tube. The empty tube was cooled and weighed.

Mercury in Mercuric Chloride.—The percentage of mercury in a commercial pure specimen of mercuric chloride was determined by the above method:

- (1) 0.8097 gave 0.5957 Hg. Found: Hg=73.57. Calc., Hg=73.88 per cent.
(2) 0.9950 gave 0.7358 Hg. Found: Hg=73.94. Calc., Hg=73.88 per cent.

Mercury in Mercuric Sulphide.—On trying this method with the sulphide it was not found possible to retain all the sulphur by the mixture of iron and quicklime. It was found that accurate results were obtained when lead chromate was also added. A mixture of one part of quicklime, two parts of iron filings, and one part of powdered lead chromate gave satisfactory results with both mercuric sulphide and iodide. The following results were obtained:

(1) A pure specimen of mercuric sulphide was prepared by precipitation, and free sulphur removed by extraction with boiling carbon disulphide:

0.6352 gave 0.5447 Hg.

Found: Hg=85.75. Calc., Hg=86.22 per cent.

(2) With a specimen of black mercuric sulphide:

0.6278 gave 0.5385 Hg.

Found: Hg=85.78. Calc., Hg=86.22 per cent.

Mercury in Cinnabar.—The amount of mercury in a sample of cinnabar was found by the sulphide method to be 59.06 per cent.:

0.8303 gave 0.4880 Hg. Found: Hg=58.77 per cent.

Mercury in Mercuric Iodide.—The following results were obtained with a pure dry specimen:

(1) 0.5878 gave 0.2593 Hg.

(2) 0.7704 „ 0.3398 Hg.

Found: Hg=44.11. Calc., Hg=44.14 per cent.

These results show that the method is accurate, and we have found it convenient and easy in practice. For the estimation of mercury in a mixture of unknown composition, 0.5 to 1.0 gram should be heated in the manner described with 2.5 to 3.0 grams of the iron, quicklime, and lead chromate mixture.

Organic Chemistry.

Magnesium in Organic Chemistry. VICTOR GRIGNARD (*Bull. Soc. chim.*, 1913, [iv], 13, i—xxxvii).—An address delivered to the Chemical Society of France on February 13th, 1913. T. A. H.

Synthesis of Methane by Catalysis. VLADIMIR N. IPATIEV (*J. pr. Chem.*, 1913, [ii], 87, 479—487; *J. Russ. Phys. Chem. Soc.*, 1913, 45, 433—442).—According to the author the synthesis of methane from its elements in the presence of metals is not a direct combination of the elements, but consists in a catalytic oxidation of the carbon, by means of the metallic oxide contained in the metal, to carbon dioxide, which then undergoes a catalytic reduction to methane, the water formed in the latter reaction being subsequently decomposed by the metal with the regeneration of the metallic oxide.

In support of this view, the author describes a series of experiments showing (1) that methane is formed by heating carbon at 500—520° in hydrogen under pressure and in the presence of metallic oxides (nickel, copper, tin, iron); (2) that metallic nickel, containing 98.41% of the metal and not further reducible, brings about the catalytic synthesis of methane from carbon and hydrogen under pressure at 500—510°, the amount of methane formed being far greater than that corresponding with the carbon dioxide which could be formed from the oxygen in the apparatus or combined with the metal; (3) that methane in the presence of nickel and water is decomposed under pressure at 485—520° with the formation of hydrogen and carbon dioxide, and (4) that the latter reaction is reversible, a mixture of carbon dioxide and hydrogen, when heated under pressure in the presence of metallic nickel or copper, or the oxides of these metals, yielding water and methane. F. B.

The Relation between the Crystal-Symmetry of the Simpler Organic Compounds and their Molecular Constitution. I. WALTER WAHL (*Proc. Roy. Soc.*, 1913, A, 88, 354—361).—This paper simply contains the experimental data concerning the aliphatic hydrocarbons; general conclusions will be given later. Methane crystallises in the regular system (compare A., 1912, ii, 1044). The crystallographic systems of other hydrocarbons are as follows: ethane, hexagonal; propane is polymorphic, giving rhombic, prismatic needles which, with rise in temperature, give crystals which are either rhombic or monoclinic; β -methylpropane is possibly rhombic, but the matter is uncertain; $\beta\beta$ -dimethylpropane gives cubical crystals, which at low temperature change into crystals which are probably tetragonal; *n*-butane is hexagonal, changing at a temperature close to that of liquid air to rhombic crystals; *n*-pentane is rhombic; *n*-hexane is either monoclinic or triclinic, probably the former; *n*-heptane and *n*-octane are either monoclinic or triclinic, it is uncertain which.

T. S. P.

Polymerisation of Ethylene at High Temperature and Pressure in the Presence of Catalysts. VLADIMIR N. IPATIEV and O. RUTALA (*Ber.*, 1913, 46, 1748—1755. Compare A., 1911, i, 937).—In a previous paper (*loc. cit.*), it has been shown that the presence of alumina does not affect the nature of the products formed by the polymerisation of ethylene, but has a marked influence on their relative amounts. The present work was undertaken to test the influence of zinc chloride and aluminium chloride.

Ethylene readily undergoes polymerisation when heated under a pressure of about 70 atmospheres at 275° in the presence of zinc chloride. The residual gas has the composition: C_nH_{2n} , 36%, H_2 , 3%, C_nH_{2n+2} , 61%. The liquid products were fractionated, and those boiling below 85° found to consist mainly of pentane and hexane, isopentane being isolated from one of them in an approximately pure state. Methylcyclobutane was not detected. In the fractions of b. p. 50—300°, the proportion of ethylenic hydrocarbons increases regularly with increasing temperature, whilst those boiling below 145° contain only ethylene and saturated hydrocarbons.

The individual fractions were treated with fuming sulphuric acid and the residue again fractionated, all the fractions so obtained being unacted on by nitrating mixture or permanganate. Those boiling below 130° consisted almost entirely of paraffin hydrocarbons; in those of higher b. p. an increasing quantity of polymethylene hydrocarbons was found, so that the fraction b. p. 256—265° contained practically only naphthenes.

The portion of the original product of b. p. above 280° was distilled under diminished pressure. The fractions obtained were uniform in ultimate composition and consisted of a mixture of ethylene hydrocarbons and naphthenes.

Ethylene is scarcely affected by commercial aluminium chloride at 240° and about 70 atmospheres pressure. At 280° it gives a charred residue and a gas having the composition C_nH_{2n} , 4.0%, H_2 , 10.0%, C_nH_{2n+2} , 86%. With freshly prepared aluminium chloride at 200°, liquid products were not obtained, and only a charred residue remained in the apparatus; liquid products were, however, prepared at the ordinary temperature. These were fractionated as before, and, after removal of unsaturated hydrocarbons by means of fuming sulphuric acid, again distilled, when the fractions, b. p. below 200°, were found to consist mainly of paraffin hydrocarbons, naphthenes being only present in the portion, b. p. above 200°. The polymerisation of ethylene in the presence of aluminium chloride yields, therefore, considerably less naphthenes than with zinc chloride as catalyst. H. W.

Δ^7 -Hexatriene. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1184—1187. Compare van Romburgh and Dorssen, A., 1906, i, 130, 722).—A specimen of Δ^7 -hexatriene which had been preserved for five years was distilled, when fully 50% passed over below 80° (the hydrocarbon has b. p. 78.5—80°/766 mm.). From the residue a substance, b. p. 99.5°/16mm., D_{20}^{25} 0.880, n_D^{25} 1.51931, was isolated, which appears to be a dimeride of hexatriene. It readily forms an additive product with bromine (1 mol.), whilst, on further

addition of the latter reagent, much hydrogen bromide is evolved. It is rapidly oxidised by potassium permanganate.

[With MÜLLER.]— $\Delta^{\alpha\gamma}$ -Hexatriene has been regenerated from its crystalline dibromine additive compound (*loc. cit.*). A solid compound has also been obtained from $\Delta^{\alpha\gamma}$ -hexatriene and sulphur dioxide, investigation of which is incomplete, but from which the hydrocarbon may also be regenerated. The latter has also been prepared by dehydration of $\Delta^{\alpha\gamma}$ -hexadiene- δ -ol by the action of potassium hydrogen sulphate or phthalic anhydride.

[With LE HEUX.]— $\Delta^{\alpha\gamma}$ -Hexadiene- δ -ol has been prepared by the action of allyl bromide, zinc turnings, and absolute ether on acraldehyde. It has b. p. 132.5—132.4°/769 mm., D_4^{20} 0.8698, n_D^{20} 1.45231. With acetic anhydride and a drop of sulphuric acid, it yields the corresponding acetate, b. p. 151.2—152.7°. Phosphorus tribromide converts it into the bromide, b. p. 59—63°/35 mm., which very readily absorbs bromine (1 mol.); further quantities of bromine react very slowly without yielding, however, hydrogen bromide.

By reduction of the chloroacetin of δ -divinyl glycol with a copper-zinc couple in ethereal solution with addition of hydrochloric acid, a liquid, b. p. 77—81°, has been obtained, which, when strongly cooled, becomes crystalline and consists very probably of $\Delta^{\alpha\gamma}$ -hexatriene. With bromine it gives a dibromide identical with that obtained from the said hydrocarbon.

H. W.

Preparation of Chloro-derivatives of the Amyl Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 258555).—When the vapour of β -methyl- Δ^2 -butylene and chlorine are allowed to react at the ordinary temperature and under a pressure of about 50 mm., they give rise to tertiary isomyl chloride and other products which can be employed for the preparation of isoprene.

F. M. G. M.

Preparation of Dihalogenated Hydrocarbons. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 259192. Compare this vol., i, 583).—Dichloroisohexane (b. p. 155—160°) is obtained when the vapour of tertiary chloroisohexane is treated with chlorine under reduced pressure; dichloroisobutane (b. p. 108—109°) is prepared in a similar manner from chloroisobutane, whilst if tertiary bromoisobutane (b. p. 72°) is employed it furnishes a satisfactory yield of chlorobromoisobutane.

F. M. G. M.

Physical Constants of Certain Chlorinated Hydrocarbons Employed as Solvents. II. WALTER HEERZ and W. RATHMAN (*Chem. Zeit.*, 1913, 37, 621—622).—The following freezing point and specific heat data are recorded: s -tetrachloroethane -36° , 0.263; pentachloroethane -22° , 0.266; trichloroethylene -73° , 0.223; tetrachloroethylene -19° , 0.216. The specific heats refer to 20°.

Commercial dichloroethylene consists of a mixture of the *cis*- and *trans*-forms, which can be separated by fractional distillation. The *cis*-form boils at 48.8°/763 mm.; its density is given by the equation: $D = 1.2908 - 0.00168t$, and its coefficient of expansion is 0.00136. The *trans*-form boils at 59.8°/763 mm.; its density is

3 a 2

given by $D = 1.3144 + 0.001605t$, and its coefficient of expansion is 0.00127.

The vapour pressures of the two isomerides have also been determined at a series of temperatures. By substitution of the data in Clausius's equation, the latent heat of vaporisation of the *cis*-form is found to be 6930 cal. ($43-48.8^\circ$), and that of the *trans*-form 7268 cal. ($54.8-59.8^\circ$).
H. M. D.

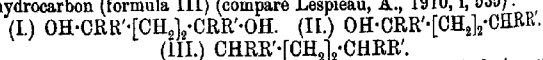
Some New Properties of Carbon Tetraiodide and its Estimation in Presence of Iodoform. MARCEL LANTENOS (*Compt. rend.*, 1913, 156, 1629—1631. Compare this vol., i, 583).—Carbon tetraiodide is attacked by hydrogen at 100° , giving iodoform and hydrogen iodide, and at the same time small amounts of di-iodomethane and methyl iodide are formed. This hydrogenation is readily brought about by alcoholic potassium hydroxide at $30-40^\circ$, a small quantity of methane being present in the product. Sodium in liquid ammonia reacts with carbon tetraiodide (3 mols.), giving methane (1 mol.), together with some sodium cyanide, methylamine, and another base, probably guanidine.

Oxygen readily attacks carbon tetraiodide, even in the dark, giving iodine and carbonyl iodide, which is unstable, and yields carbon monoxide with a small proportion of carbon dioxide, the reaction being facilitated by light.

Silver nitrate in aqueous solution (20%) reacts with iodoform, giving carbon monoxide quantitatively. With carbon tetraiodide, it gives both carbon monoxide and carbon dioxide in the proportion of 3:1 by volume. One molecule of the tetraiodide gives one molecule of gas, thus giving a means of estimating it alone or in the presence of iodoform.
W. G.

Density and Thermal Expansion of Ethyl Alcohol and its Mixtures with Water. N. S. OSBORNE, E. C. MCKELVY, and H. W. BEARCE (*J. Franklin Inst.*, 1913, 175, 165—167. Compare A., 1912, i, 232).—An abstract of, with a short discussion on, a paper by Pulfrich (*Zeit. für Inst. K.*, 13, 456), describing different methods of purifying ethyl alcohol, and the varying physical constants exhibited by different specimens thus obtained with an investigation on the thermal expansion of the same when diluted with varying proportions of water.
F. M. G. M.

Catalytic Hydrogenation of Acetylenic γ -Glycols in the Presence of Palladium-black. GEORGES DUPONT (*Compt. rend.*, 1913, 156, 1623—1625).—The reduction of acetylenic γ -glycols in the presence of platinum-black gives the saturated glycol (formula I) together with the alcohol (formula II), but never any of the saturated hydrocarbon (formula III) (compare Lespieau, A., 1910, i, 535):

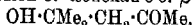


If for the platinum-black is substituted palladium-black, in most cases the product of hydrogenation contains only traces of the

glycol with a little of the alcohol, and large quantities of the hydrocarbon.

In the case of the aliphatic glycols of the type dimethylbutinenediol, the hydrogenation is limited and the result is a mixture of the three possible products. With the aromatic glycols, whilst platinum-black gives only the saturated glycol (formula I), palladium-black gives only the saturated hydrocarbon (formula III); thus diphenyldimethylbutinenediol gives quantitatively *β*-diphenylhexane, a colourless liquid, b. p. 185°/12 mm., D^{15}_D 0.9634, n_D 1.5440. W. G.

Preparation of Mesityl Oxide from Diacetone Alcohol [*iso*-Hexan-δ-ol-β-one]. MORITZ KOHN (*Monatsh.*, 1913, 34, 779—780).—The conversion of *iso*hexan-δ-ol-β-one,



the primary product in the condensation of acetone to mesityl oxide, into mesityl oxide does not require a large quantity of sulphuric acid as previously supposed. When 290 grams of *iso*hexan-δ-ol-β-one to which sixty drops of sulphuric acid have been added are quickly distilled through a fractionating column, the distillate contains about 190 grams of mesityl oxide. D. F. T.

Action of α-Monochlorohydrin and Epichlorohydrin on Monosodium Glyceroxide. JEAN NIVIÈRE (*Compt. rend.*, 1913, 156, 1628—1629).—α-Monochlorohydrin is readily prepared by saturating glycerol at 120—130° with hydrogen chloride, a yield of 66% being obtained. The product reacts with monosodium glyceroxide, glycerol being regenerated and at the same time 2—3% of diglyceryl alcohol is produced. Epichlorohydrin, which is readily obtained (95% yield) by the action of strong aqueous potassium hydroxide on α-dichlorohydrin under reduced pressure, reacts with monosodium glyceroxide, giving a *polymeride* of the internal anhydride of the diglyceryl alcohol. This is a white, amorphous substance, insoluble in water and the ordinary solvents, and yields a *diacetyl* derivative on boiling with acetic anhydride and anhydrous sodium acetate. Both of these substances decompose without melting. W. G.

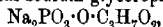
Preparation of Diglyceryl Alcohol. JEAN NIVIÈRE (*Compt. rend.*, 1913, 156, 1776—1778. Compare preceding abstract).—In an attempt to prepare diglyceryl alcohol the author has prepared the diacetyl derivative of monochlorohydrin and caused it to react with monosodium glyceroxide, the product being a small quantity of the diacetyl derivative of the required alcohol and a considerable residue analogous to the vegetable mucilages.

By warming the internal anhydride of glycerol with anhydrous glycerol in equimolecular proportions on a water-bath for seven hours and acetylating the crude product with acetic anhydride, the *tetracetyl* derivative of the required alcohol is obtained as an oily liquid, b. p. 196—197°/3 mm., D^{17}_D 1.1835. On saponification with alcoholic sodium hydroxide it yields *diglyceryl alcohol*, $\text{C}_6\text{H}_{14}\text{O}_5$, a pale yellow, very viscous liquid, b. p. 235—240°/6 mm. W. G.

Efficiency of the Preparation of Ethyl Ether from Alcohol and Sulphuric Acid. PERCY N. EVANS and LENA M. SUTTON (*J. Amer. Chem. Soc.*, 1913, 35, 794—800).—An account is given of experiments made with a view to determine the efficiency of the reaction between ethyl alcohol and sulphuric acid. It has been found that the degree of completeness of the reaction $2\text{Et}\cdot\text{OH} = \text{Et}_2\text{O} + \text{H}_2\text{O}$ amounts to about 40%. This efficiency was maintained in some experiments until the distillate amounted to as much as one hundred and seventy-six times the original volume of the sulphuric acid, or until the ether produced was forty times the volume, or sixteen times the weight, of the acid used. The efficiency decreased abruptly when there remained in the flask a charred, semi-solid residue of about one-twentieth of the weight of the acid originally present. The decrease in efficiency is not due to accumulation of water, as the reaction proceeds normally with dilute sulphuric acid. From 15—20% of the sulphuric acid is lost as sulphur dioxide.

E. G.

Crystalline Glycerophosphates. ROGIER and FIORE (*Chem. Zentr.*, 1913, i, 1330—1332; from *Bull. Sci. Pharmacol.*, 1913, 20, 7—25, 72—86).—Technical sodium glycerophosphate,



usually forms small needles with $5\text{H}_2\text{O}$, but sometimes large tablets with $6\text{H}_2\text{O}$. The concentrated solution at 18° contains 27.38% anhydrous salt, and may be heated to 120° without decomposition. Cryoscopic methods gave one-third of the calculated molecular weight, so a physiological serum should only contain 35 grams. The following salts have been made by double decomposition. *Calcium salt*, $\text{CaPO}_3\cdot\text{O}\cdot\text{C}_3\text{H}_7\text{O}_2$, microcrystalline or large crystals by slow evaporation, solubilities, 1% at 0° , 1.68% at 18° , 0.43% at 60° ; *barium salt*, with $1\text{H}_2\text{O}$ which is lost on boiling the solution, solubility 4.50% at 21° ; *strontium salt*, leaflets with $2\text{H}_2\text{O}$, solubility 2.09% at 19° , 0.80% at 60° ; *guinine salt*, $\text{B}_2\text{PO}_3\cdot\text{O}\cdot\text{C}_3\text{H}_7\text{O}_2 + 4\text{H}_2\text{O}$, white needles, m. p. $180\text{—}181^\circ$, $[\alpha]_D^{25} = 133^\circ 33'$, $[\alpha]_D^{17} = 140^\circ 24'$; *acid strychnine salt*, $\text{BPO}_3\cdot\text{H}\cdot\text{O}\cdot\text{C}_3\text{H}_7\text{O}_2\cdot\text{H}_2\text{O}$, m. p. 260° , $[\alpha]_D^{25} = 25^\circ 40'$; *brucine salt*, $\text{B}_2\text{PO}_3\cdot\text{O}\cdot\text{C}_3\text{H}_7\text{O}_2\cdot 11\text{H}_2\text{O}$, prisms, m. p. 192° , $[\alpha]_D^{25} = 29^\circ 35'$; *basic copper salt*, $\text{Cu}[(\text{Cu}\cdot\text{OH})\text{PO}_3\cdot\text{O}\cdot\text{C}_3\text{H}_7\text{O}_2]_2\cdot 6\text{H}_2\text{O}$, dark blue powder; *copper salt*, $\text{CuPO}_3\cdot\text{O}\cdot\text{C}_3\text{H}_7\text{O}_2\cdot\text{H}_2\text{O}$, pale blue needles.

J. C. W.

Oxidation of Lecithin in Presence of Iron Salts. OTTO WARBURG and OTTO MEYERHOF (*Zeitsch. physiol. Chem.*, 1913, 85, 412—414).—The mixture of substances known as lecithin is very readily oxidised by atmospheric oxygen in aqueous suspension in presence of iron salts, whereas other important cell constituents are stable under similar conditions. There is a close parallelism between the velocity of lecithin oxidation in vitro and the rate of the oxidation processes in the living cell based on the amount of lecithin present.

E. F. A.

The Action of Alkali Arsenite on Ethyl Disulphide. AUGUST GUTMANN (*Ber.*, 1913, 46, 1474—1475).—Weinland and Rumpf (*A.*, 1897, ii, 257) have shown that sodium disulphide acts on trisodium

arsenite with the formation of trisodium monothioarsenate, $\text{Na}_3\text{AsO}_3\text{S}$, and sodium sulphide. It was to be expected that ethyl disulphide would act similarly to the sodium disulphide, if it entered into reaction at all, but the author finds that this is not the case, the reaction proceeding readily in the cold with the formation of trisodium arsenate and ethyl mercaptan. This reaction is explained by the author by assigning a peroxide character to the ethyl disulphide, which takes hydrogen from the water, leaving oxygen available for oxidising the arsenite.

T. S. P.

Hexadecanesulphonic Acid. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1913, 27, 110—113. Compare A., 1912, i, 600).—Cetyl iodide reacts with sodium hydrogen sulphide in alcoholic solution to give *cetyl mercaptan*, $\text{C}_{16}\text{H}_{33}\text{SH}$, which is precipitated as a yellow solid on the addition of water, and on warming this with potassium permanganate solution it is oxidised to the sulphonic acid. The manganese dioxide is filtered off, the solution neutralised with acetic acid, and a slight excess of lead acetate added. The precipitated lead salt is collected, washed, dried, suspended in alcohol, and decomposed by hydrogen sulphide. After filtering and evaporating off the alcohol, *cetylsulphonic* [*hexadecanesulphonic*] acid, $\text{C}_{16}\text{H}_{33}\text{SO}_3\text{H}$, is obtained, soluble in alcohol, ether, benzene, and acetic acid, crystallising from the latter in microscopic plates. It behaves like a semi-hard soap, and is a comparatively strong acid, yielding *sodium* and *potassium* salts, which are soluble in water, and closely resemble the alkali palmitates in their behaviour. The *barium* and *lead* salts are insoluble in water.

W. G.

The Physico-chemical Properties of Hexadecanesulphonic Acid and Sodium Hexadecanesulphonate. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1913, 27, 113—128. Compare preceding abstract).—Hexadecanesulphonic acid and its sodium salt in aqueous solution possess the property of emulsifying with toluene, but, unlike the oleates, are only very slightly extracted by that solvent. On the other hand, they possess the property of removing fat from, and cleansing wool in the same manner as, an ordinary soap. The elevation of the boiling point of water on solution either of the acid or its salt does not bear any relation to the concentration of the solutions, and this method gives a wide range of values for the molecular weights. The author has made a complete study of the electrical conductivity of the sodium salt and the free acid at different temperatures and varying concentrations. In the case of the sodium salt, the readings give a sharp indication of the temperature, 38—37°, at which crystallisation takes place. The values obtained for the molecular conductivity in solutions from 0.01665*N* to 0.0666*N* are practically independent of the concentration. The free acid furnishes an excellent example of a colloidal substance, and permits of the direct examination of the molecular problem and of an intermolecular liquid. The values obtained for the molecular conductivity diminish steadily as the dilution passes from 15 to 30 litres, remains constant from 30 to 60 litres, and finally increases regularly and proportionately as the dilution increases.

W. G.

The Use of Calcium Carbonate as Catalyst for Organic Acids and their Anhydrides. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1913, 156, 1730—1734).—Precipitated calcium carbonate can be employed as a catalyst at 450—500° for the conversion of acids into the ketones, but in the acetic acid series the yield diminishes as the molecular weight increases. Whilst acetic acid gives a theoretical yield of propanone, valeric acid only gives a yield of 32% of dibutyl ketone. Despite blackening due to deposition of carbonaceous products, the calcium carbonate retains its activity and can be employed a great number of times, but its use is not so advantageous as that of thorium oxide (compare Senderens, A., 1912, i, 537) for the higher ketones. Benzoic acid mixed with the aliphatic acids yields mixed ketones under the above conditions. The acids can be replaced by their anhydrides in every case, and whilst benzoic acid alone cannot be converted into benzophenone by this method, a certain amount of this ketone can be obtained by the use of benzoic anhydride.

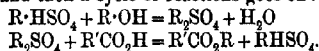
W. G.

Esters Derived from Octanol by the Author's Method; Observations on the Principle of this Method. JEAN B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1913, 156, 1620—1623; *Bull. Soc. chim.*, 1913, [iv], 13, 586—591).—By their method using sulphuric acid (2—3%) as catalyst (compare A., 1911, i, 600, 637; ii, 1080; 1912, i, 694; this vol., i, 42) the authors have prepared the following esters of octanol, of which only the acetate was previously known (compare Bouis, this Journ., 1854, 7, 280):

Ester.	B. p./74·4 mm.	D ₄ ¹⁵ .
Formate	184·0°	0·8642
Acetate	194·5	0·8626
Propionate	211·5	0·8611
Butyrate	227·5	0·8592
isoButyrate	220·0	0·8554
isoValerate	236·5	0·8540

The *phenylacetate*, b. p. 195°/35 mm., D₄¹⁵ 0·9503, is decomposed on distilling at the ordinary pressure.

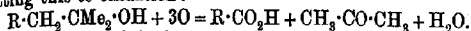
The authors claim that their method is entirely distinct from that of Fischer and Speier (A., 1896, i, 201), where a large excess of alcohol is used and stronger acid, which merely acts as a dehydrating agent. The organic acids are capable of division into two classes. The first contains the aromatic acids with the carboxyl group attached to the nucleus, in which case their method is useless. The second class contains the fatty acids and aromatic acids with the carboxyl group in a side-chain, and here their dilute acid acts as a true catalyst and an excess of alcohol is unnecessary. A compound of the type $\text{RH}\cdot\text{SO}_3$ is first formed, and then a cycle of reactions goes on:



W. G.

Graded Degradation of Different Saturated Mono- and Di-basic Acids. PHILIPPE BARBIER and RENÉ LOCQUIN (*Compt. rend.*, 1913, 156, 1443—1446).—The transformation of a saturated acid of the

type $R \cdot CH_2 \cdot CO_2H$ into its next lower homologue can be brought about by first converting the acid into the corresponding tertiary alcohol, $R \cdot CH_2 \cdot CMe_2 \cdot OH$, by the action of magnesium methyl iodide, and then submitting this to oxidation:



Thus *isovaleric acid* is first converted into $\beta\delta$ -dimethylpentan- δ -ol, which on oxidation with chromic acid yields *isobutyric acid*. Decanoic acid is similarly converted into pelargonic acid.

By the interaction of *isoamyl bromide* and *ethyl methylmalonate*, $\alpha\delta$ -dimethylhexoic acid, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CO_2H$, b. p. 228—230°/760 mm. and 127—130°/18 mm., is obtained, giving a *methyl ester*, b. p. 172—173°, an *acid chloride*, b. p. 69°/16 mm., an *amide*, m. p. 99—100°, and a *p-toluidide*, m. p. 75°. With magnesium methyl iodide it yields $\beta\gamma\delta$ -trimethylheptan- β -ol, b. p. 92—95°/18 mm., which on oxidation with dilute nitric acid gives a neutral and an acid product. The acid product is a mixture of acetic, *isovaleric*, and *isohexoic acids*, whilst the neutral product consists principally of methyl *isoamyl ketone*, together with a small quantity of an unsaturated hydrocarbon, b. p. 160—165°. β -Methyladipic acid on treatment with magnesium methyl iodide and subsequent oxidation yields a certain amount of methylsuccinic acid and some diethylenic hydrocarbon.

With the monobasic acids where the $\cdot CO_2H$ group is attached to a $\cdot CH_2$ group, they are simply converted into their next lower homologue. With an α -substituted acid the principal product is a ketone. The dibasic acids behave in the same way as the monobasic acids, the degradation proceeding simultaneously on the two terminal carboxyl groups.

W. G.

Synthesis of the Glycerides of Lauric Acid. B. W. VAN ELDIK THIEME (*Ber.*, 1913, 46, 1653—1657. Compare A., 1912, i, 333).—A reply to Grün (this vol., i, 157), criticising the latter's experimental results. The author re-affirms that even under the modified conditions stated by Grün (*loc. cit.*) the so-called synthesis of α -dilaurin yields a mixture of trilaurin, crystalline dilaurin, liquid dilaurin, and monolaurin.

D. F. T.

Nickel Oxides as Reduction Catalysts in the Addition of Molecular Hydrogen to Unsaturated Fats and Fatty Acids. FRED BEDFORD and ERNST ERDMANN (*J. pr. Chem.*, 1913, [ii], 87, 425—455; *J. Russ. Phys. Chem. Soc.*, 1913, 45, 616—643).—Unsaturated fats and fatty acids undergo catalytic reduction at the ordinary pressure in the presence of nickel oxide, the rate of reduction being much greater than when metallic nickel is employed. In addition to its greater activity, the oxide possesses the advantage over the metal in that it is far less sensitive to hydrogen sulphide and other substances which exert a deleterious effect on the activity of the metal. All three oxides of nickel may be used as catalysts, nickelous and nickelic oxides requiring a temperature of 250°, whilst in the presence of the suboxide the reduction proceeds readily at 180—200°.

During the reduction, the higher oxides become converted into the suboxide, which forms a deep black, colloidal solution with the oil or fat.

Nickel suboxide may be distinguished from metallic nickel by its inability to form nickel carbonyl with carbon monoxide, and by its much smaller electric conductivity.

A nickelic oxide, which has already been used in the catalytic reduction, possesses a greater activity than a fresh specimen on account of the presence of suboxide.

The velocity of hydrogenation is increased by employing a voluminous oxide, prepared by gentle ignition of the nitrate, and also by the addition of small quantities of other metallic oxides (Al, Ag, Zr, Ti, Ce, La, Mg).

Nickel salts of organic acids (formic, acetic, oleic, and linolenic) in the presence of unsaturated fats are reduced at 200–250° to the oxide or to metallic nickel, and may therefore be used as catalysts; thus, nickel formate is reduced at 210° to the suboxide and at 250° to metallic nickel.

F. B.

Ricinoleic Acid. BERTHOLD RASSOW [with J. RUBINSKY] (*Zeitsch. angew. Chem.*, 1913, 26, 316–320).—The authors have investigated the action of heat on ricinoleic acid. Since the products formed are amorphous, yield amorphous salts, and have very similar solubilities, their isolation in the pure state has not been accomplished. Their chemical nature is deduced from observations of acid number, saponification number, acetyl number, iodine number, and molecular weight. The following are the main results obtained.

Ricinoleic acid is decomposed at temperatures below 150°, water being the only volatile product formed. At the same time, the acidity sinks to half the original value; in the presence of a trace of sulphuric acid, the acidity can be reduced to one-quarter of the original value, but completely neutral products are never obtained.

Polyricinoleic acids (ester-acids in which the alcoholic hydroxyl group of one molecule is esterified by the carboxyl group of a second molecule) are the sole products of the action of heat on ricinoleic acid. Such products are not uniform, but contain a mixture of difficultly or non-separable polyricinoleic acids with more or less of the original acid. Polyricinoleic acids of high molecular weight are insoluble in alcohol, whilst their barium salts resemble amber and are soluble in ether; those of lower molecular weight are soluble in alcohol, whilst their barium salts dissolve sparingly in ether. A complete separation of the individual polyricinoleic acids was not achieved.

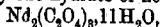
The effect of a variety of substances on the course of the reaction has been investigated. Chlorides of organic acids and neutral salts which do not yield free acid under the conditions of the experiments have but little effect. Traces of strong acids, particularly sulphuric acid, act as positive catalysts, whilst organic bases have the opposite action.

Ricinelaiddic acid behaves in the same manner as ricinoleic acid except that it is more readily decomposed by heat.

H. W.

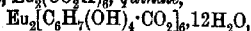
Neodymium Oxalate and Some New Compounds of Europium. CHARLES JAMES and J. E. ROBINSON (*J. Amer. Chem. Soc.*, 1913, 35, 754–759).—A study of the solubility of neodymium

oxalate in solutions of neodymium nitrate of various concentrations at 25° has shown that only one hydrate of neodymium oxalate,

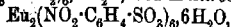


is stable under these conditions. Evidence was obtained of the formation of an oxalonitrate.

Europium formate, $\text{Eu}_2(\text{CO}_2\text{H})_6$, *guinate*,



pyromucate, $\text{Eu}_2(\text{C}_4\text{H}_3\text{O}_2\text{CO}_2)_6 \cdot 2\text{H}_2\text{O}$, and *m-nitrobenzenesulphonate*,



are described.

E. G.

The Action of Ultraviolet Rays on Aldehydes. ADOLF FRANKF and ERNST POLLITZER (*Monatsh.*, 1913, 34, 797—809).—When exposed to the radiation from a quartz-mercury lamp, formaldehyde solutions undergo partial decomposition into carbon monoxide, carbon dioxide, hydrogen and methane, and partial polymerisation to glycolaldehyde and higher products (Pribram and Franke, A., 1912, i, 412); the higher aldehydes have been observed to form carbon monoxide, hydrogen, and the hydrocarbon corresponding with the radicle to which the aldehyde group was previously attached (Berthelot and Gaudechon, A., 1910, ii, 814). A re-investigation of the behaviour of the homologues of formaldehyde indicates that they decompose mainly according to the equation $\text{R} \cdot \text{CHO} = \text{RH} + \text{CO}$; at the same time condensation takes place to some extent accompanied by polymerisation to resinous substances; no pure condensation product could be isolated. Under the conditions of the experiments, in which moisture and atmospheric oxygen were excluded, no formation of acids or of esters could be detected, so that the earlier suggestion of Pribram and Franke (*loc. cit.*) that the formic acid obtained in the illumination of formaldehyde solution is produced by the hydrolysis of previously formed methyl formate is hardly probable. From the behaviour of crotonaldehyde, which like benzaldehyde and cinnamaldehyde gives practically no liberation of gas, it appears that the decomposition expressed by the above equation is characteristic of the saturated aliphatic aldehydes.

The aldehyde under examination was contained in a quartz flask of approximately 100 c.c. capacity which was filled to the neck, any evolved gas being collected over water or mercury; the mercury lamp was at a distance of 2 to 3 mm. from the flask, but the temperature of the aldehyde never exceeded 50°.

The substances examined were heptaldehyde, isobutaldehyde, propaldehyde, acetaldehyde, crotonaldehyde, benzaldehyde, and cinnamaldehyde. Crotonaldehyde gave only the formation of a resinous substance, whilst the two aromatic aldehydes gave merely red, non-volatile products. The illumination ranged from one to ten days in various cases; only a relatively small proportion of each aldehyde underwent conversion.

D. F. T.

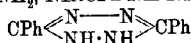
Action of Hydrazine and Hydrazine Derivatives on Molten Chloral Hydrate. GUSTAV KNÖPFER (*Monatsh.*, 1913, 34, 769—777).—Hydrazine reacts with solutions of chloral hydrate, giving an additive product, $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{NH} \cdot \text{NH}_2$, chloralhydrazine (compare A., 1911,

i, 1033); it is now found that if hydrazine sulphate or hydrochloride is dissolved in an excess of molten chloral hydrate, needles of a substance, m. p. 187° (decomp.), separate, but the composition is $C_6H_5ON_2Cl_3$, instead of $C_6H_5ON_2Cl_2$, which would be expected from a simple condensation such as that producing anhydrochloralurethane (Feist, A., 1912, i, 566).

The reaction product of benzalazine and chloral hydrate, obtained in a manner similar to the above, has the composition $C_6H_5ON_2Cl_3$, which is again two hydrogen atoms short of the formula for a substance produced by mere condensation; the substance, leaflets, m. p. 185° , when heated with potassium hydroxide solution loses a molecule of hydrogen chloride, giving a substance, $C_6H_5ON_2Cl_2$, needles, m. p. 86° . The former of these substances is not identical with the isomeric chloralbenzoylhydrazone, $CCl_3 \cdot CH \cdot N \cdot NH \cdot Bz$ (Stollé, A., 1905, i, 94), and, as it does not yield chloroform when treated with alkali, it is not likely to be the trichloroacetylhydrazone of benzaldehyde,



The loss of the two hydrogen atoms in each case is possibly due to a similar cause to the loss observed by Pinner (A., 1894, i, 385) where the continued action of hydrazine on the imino-ester of benzoic acid gives rise to $NH \cdot CPh \cdot NH_2$, $NH \cdot CPh \cdot NH \cdot NH \cdot CPh \cdot NH$, and



successively. The structure of the above products, however, remains for the present unsettled.

D. F. T.

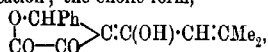
Keto-enolic Tautomerism. VIII. Formation of Derivatives of Tautomeric Compounds. KURT H. MEYER (*Annalen*, 1913, 398, 49—65. Compare A., 1912, i, 940, 941).—To the terms "tautomerism," introduced by Laar in connexion with his oscillation theory, and "desmotropy" some confusion has become attached in the course of time and with the increase in the number of examples. The author proposes the following definitions. A substance exhibits tautomerism when it yields two series of derivatives obtained from two isomeric forms differing in the position of a hydrogen atom, and of one or more double linkings. According to the nature of the two isomeric forms, special cases of tautomerism are: (i) desmotropy—the free compounds corresponding with both forms are capable of separate existence or can be separately detected; (ii) pseudomerism—the tautomeric substance is known in only one form, the constitution of which can be determined by methods independent of tautomerism, and which can yield by addition or substitution derivatives of both forms: the other form is unknown and its existence cannot be detected by any method; (iii) cryptomerism—the substance is known in only one form, the constitution of which cannot be definitely determined (by methods independent of tautomerism).

Many reactions of desmotropic substances are explained readily by the desmotropy; each form yields derivatives of its own type by ordinary double decomposition and usually one form reacts, the other being changed to the first by the reagent present. In other reactions the explanation is not so simple; the tautomeric

substance yields a mixture of derivatives of both forms or only one substance, which is generally a derivative of the non-reacting form, for example, the formation of a brominated ketone by the bromination of an enol. Two theories are existent to explain such cases. The substitution theory claims that a substance can only yield derivatives of its own peculiar constitution, and that the production of a derivative of the other form must be due to a transformation of the tautomeride which precedes the substitution. The addition theory of Michael and Nef assumes that by the direct addition of a reagent and subsequent elimination of a different molecule, a tautomeride of one form can yield derivatives of the other type.

Evidently the test of the two theories lies in the answer to the question, which of the two forms reacts? This answer can only be obtained by an examination of the behaviour of separately stable desmotropic substances. The author quotes numerous examples from his own work, and from that of Dimroth, Hinsberg, Hantzsch, and Herzog and Wenzel to show that the enolic modification is the reactive form, and that, therefore, the additive theory is probably correct.

[With S. LENHARDT.]—Keto-enolic desmotropes and also tautomerides which are known only in the ketonic or the enolic modifications condense with aldehydes (1 or 2 mols.), the resulting compounds losing water in various ways. In order to ascertain whether the ketonic or the enolic modification reacts with the aldehyde, the two desmotropic modifications of methyl mesityl oxide oxalate have been treated with benzaldehyde in the presence of a little piperidine. The ketonic modification, methyl α -diketo- ϵ -methyl- Δ^8 -hexene- α -carboxylate, m. p. 87° , is unchanged, but the enolic modification, methyl α -hydroxy- γ -keto- ϵ -methyl- $\Delta^{8,9}$ -hexadiene- α -carboxylate, is converted into the *lactone*, $\begin{matrix} \text{O-CHPh} \\ \text{CO-CO} \end{matrix} > \text{CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}_2$, m. p. 160° , colourless needles, which does not react with ferric chloride or with alcoholic bromine, and is only slowly attacked by potassium permanganate, and is, therefore, the ketonic modification; the enolic form,



obtained by dissolving the ketonic modification in cold alcoholic sodium ethoxide, diluting with water, and acidifying, has m. p. 144° , then solidifies and has m. p. 160° , reacts with alcoholic bromine or ferric chloride, and is soluble in alkalis. By prolonged boiling with alcohol and a little piperidine, the enol is converted into the ketonic form; the same change occurs when the fused enol solidifies.

The authors believe that in all desmotropic and tautomeric compounds, condensation occurs by means of the enolic modification.

C. S.

The Characterisation of Chloro-ketones. EDMOND E. BLAISE (*Compt. rend.*, 1913, 156, 1549—1551).—The most suitable method of characterising the chloro-ketones is to convert them into their semicarbazones under definite conditions, the ordinary methods being unsatisfactory. Semicarbazide hydrochloride (1 to 1.5 mols.) is dis-

solved in water and the chloro-ketone added, when the semicarbazone is rapidly formed, the only exception being methyl trichloromethyl ketone, which requires a cold alcoholic solution of free semicarbazide. Care must be taken in purification. After filtering and washing with water the semicarbazone is heated with an excess of benzene to below 50° , a little anhydrous sodium sulphate is added, the liquid filtered and left for crystallisation. The semicarbazones of the α -chloro-ketones are readily converted into those of the α -hydroxy-ketones by contact with aqueous potassium carbonate for a few hours, and into those of the α -acetoxy-ketones by warming for a few minutes with an alcoholic solution of anhydrous sodium acetate, thus giving three means of identification of the original ketone.

Dichloro-ketones of the type $\text{CHCl}_2\cdot\text{CO}\cdot\text{R}$ give a normal semicarbazone, but those of the type $\text{CRCl}_2\cdot\text{CO}\cdot\text{R}'$ give disemicarbazones, $\text{R}\cdot\text{C}(\text{N}\cdot\text{CH}_3\text{ON}_2)\cdot\text{C}(\text{N}\cdot\text{CH}_3\text{ON}_2)\text{R}'$, which are insoluble in organic solvents, except formic and acetic acids.

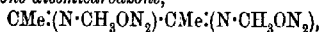
The following semicarbazones and disemicarbazones have been prepared:

Methyl trichloromethyl ketone semicarbazone, $\text{CCl}_3\cdot\text{CMe}\cdot\text{N}\cdot\text{CH}_3\text{ON}_2$, fine needles, m. p. 140° .

Dichloromethyl ethyl ketone semicarbazone, m. p. 142° .

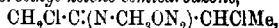
Ethylglyoxal disemicarbazone, $\text{CH}\cdot(\text{N}\cdot\text{CH}_3\text{ON}_2)\cdot\text{C}\cdot\text{Et}\cdot(\text{N}\cdot\text{CH}_3\text{ON}_2)$, m. p. above 230° .

Dimethyldiketone disemicarbazone,



a white, crystalline powder, m. p. above 230° , soluble only in formic acid.

Chloromethyl chloroethyl ketone semicarbazone,



m. p. 140° .

Methyl chloroethyl ketone semicarbazone, micaceous plates, m. p. 148° , which with carbonic acid gives the semicarbazone, m. p. 202° , of the corresponding hydroxy-ketone, and with sodium acetate gives *methyl acetoxyethyl ketone semicarbazone*, $\text{CMe}\cdot\text{C}\cdot(\text{N}\cdot\text{CH}_3\text{ON}_2)\cdot\text{CHAcMe}$, m. p. 161° .

Chloromethyl propyl ketone semicarbazone, m. p. 157° . W. G.

Mannitol Esters of Sulphuric Acid. W. R. BLOOR (*J. Amer. Chem. Soc.*, 1913, 35, 784—794).—In preparing certain mannitol esters of the higher fatty acids by heating the substance with sulphuric acid at 70° (A., 1910, i, 538; 1912, i, 532; ii, 365) unsatisfactory results were obtained, and for this reason a study has been made of the action of concentrated sulphuric acid on mannitol at 39° , 49° , 56° , and 65° .

When mannitol is dissolved in concentrated sulphuric acid, the disulphate is the principal compound produced, but a portion of the mannitol is dehydrated to the form $\text{C}_6\text{H}_6\text{O}(\text{OH})_2$. At low temperatures a levorotatory ester is produced, but at higher temperatures dextrorotatory compounds are formed together with derivatives which have lost part of their capacity to combine with acid groups. In the presence of the higher fatty acids, esters are produced, presumably

with the mannitol anhydride, but during the processes of separation they are hydrated to mannide and mannitan forms. E. G.

Acetyl-Halogen Sugar Derivatives. W. SLOAN MILLS (*Rep. Brit. Assoc.*, 1912, 444—445).— β -Iodoacetodextrose (E. and H. Fischer, A., 1910, i, 716) may be prepared by the action of dry hydrogen iodide on β -penta-acetyldextrose dissolved in dichloromethane. It is recrystallised rapidly from alcohol. Copper hydride reduces it, yielding a compound $C_{23}H_{44}O_{19}$.

β -Acetyliodogalactose is prepared in the same manner from β -penta-acetylgalactose, and has m. p. 93—94°. Octoacetylmaltose yields an iodo-derivative, m. p. 62—66°. Acetyliodolactose, from acetyl-lactose, has m. p. 142°. C. H. D.

Gentiobiose. GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1913, 85, 399—407).—Octa-acetylgentiobiose crystallises well and is relatively easily isolated from highly impure crude products. Acetylation may thus be used to obtain gentiobiose from plant products, and its preparation from gentian roots is described. Octa-acetylgentiobiose sinters at 192°, m. p. 195°, $[\alpha]_D^{20} - 5.6^\circ$. Gentiobiose is equivalent to 130 c.c. of Fehling's solution, maltose reducing 128.5 c.c. The phenylosazone crystallises in citron-yellow, stellate needles, or from hot water in short, pointed prisms, m. p. 160—170° (decomp.), $[\alpha]_D^{20} - 76.1^\circ$ in pyridine and alcohol. E. F. A.

Deflocculation of Starch and Solution of Dextrose. GIOVANNI MALFITANO and (Mile.) A. MOSCHKOV (*Compt. rend.*, 1913, 156, 1681—1684. Compare this vol., i, 593).—A further discussion of the difference between the phenomenon of deflocculation of starch and that of the solution of dextrose and a description of the difference in behaviour of solutions of these pseudo-crystals of starch and crystals of dextrose under different conditions. W. G.

Diastatic Degradation of Starch. WILHELM BILTZ (*Ber.*, 1913, 46, 1532—1536).—The degradation of potato starch under the influence of enzymes has been studied, the course of the reaction being followed qualitatively by the iodine reaction and quantitatively by the withdrawal of portions of the solution at definite intervals, addition of boiling water, and precipitation of the dextrins by the addition of so much alcohol that the mixture contained 80—90% of the latter, the treatment being repeated until the product was free from sugar. The approximate mean molecular weight of the dextrins was then determined by measurement of the viscosity of their aqueous solution (compare this vol., i, 593).

The following are the main results obtained:

The diastatic degradation of starch to sugar takes place with intermediate formation of erythro-dextrins and achroo-dextrins which are themselves ultimately transformed into sugar. The velocity of saccharification of the achroo-dextrins is smaller than that of the erythro-dextrins, and this is again smaller than that of the amylo-dextrins.

The existence of erythrodeextrins is established.

The mean molecular weights for the achroodeextrins is about 3700; for the erythrodeextrins, 6200—7000; for the amylodeextrins, above 10,000. Since purified specimens of achroodeextrin I, achroodeextrin II, and erythrodeextrin IIa have molecular weights 1800, 1200 and 3000 respectively, it would appear that, besides these and the amylodeextrins, other dextrins of high molecular weight must exist which are indifferent towards iodine and belong to the class of achroodeextrins.

Philoche's determinations of the velocity of the conversion of starch into sugar (A., 1908, i, 712; ii, 470) show that this rapidly diminishes at first, but then becomes constant when the reaction appears to be unimolecular. The author's experiments show that the first phase of the reaction is complicated by the presence of amylo- and erythrodeextrins in the mixture, and that reaction only follows a simple law when only one type of substances, namely, the achroodeextrins, are undergoing saccharification.

H. W.

Partial Hydrolysis of Cellulose. GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1913, 85, 180—191).—On treatment of cellulose with strong sulphuric acid a mixture of various depolymerised products is obtained. Even after prolonged treatment, cellobiose acetate is obtained on acetolysis and not dextrose pentacetate. Crystalline products were not obtained on acetolysis of xylan and mannan preparations or of chitin.

E. F. A.

Chemical Composition of Cork Substance. GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1913, 85, 173—179).—Cork when treated by Cross and Bevan's method with chlorine yields a product, which in its external properties and solubility resembles cellulose, but on treatment with acetic anhydride and sulphuric acid by Skraup's method gave no cellobioseocta-acetate. One hundred grams of cork meal contained about 4 grams of this cellulose-like product.

E. F. A.

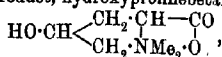
Betonicine and Turicine. ALBERT KÜNG and GEORG TRIER (*Zeitsch. physiol. Chem.*, 1913, 85, 209—216).—The mixture of betaines in *Betonica officinalis* has been resolved into two isomerides, a levorotatory base betonicine, and a dextrorotatory base turicine. Both are betaines of the natural hydroxyproline, and on exhaustive methylation of this compound the same mixture of the two betaines is obtained as exists in *Betonica officinalis*, *Stachys silvatica*, etc. According to the method of isolation sometimes one and sometimes the other isomeride has been isolated, in reality both are present.

Betonicine crystallises in four-sided, stunted pyramids, m. p. 243—244° (decomp.). It reacts neutral, tastes sweet, and has $[\alpha]_D^{15} - 36.6^\circ$. The *hydrochloride* crystallises in lustrous prisms, m. p. 222—223° (decomp.), $[\alpha]_D^{15} - 24.79^\circ$. The *aurichloride* separates in dull yellow-coloured plates aggregated in fan-shaped clusters, m. p. 242°. The *platinichloride* forms short prisms, m. p. 226°.

Turicine crystallises in long, transparent, lustrous, flat prisms, or in slender, glistening needles, m. p. 249° (decomp.), $[\alpha]_D + 36.26^\circ$. It tastes sweet and is not hydroscopic. The *hydrochloride* crystallises in slender, lustrous needles, m. p. 223°, and reacts acid, $[\alpha]_D + 24.65^\circ$.

The *aurichloride* is a yellow powder crystallising in obliquely-cut, lustrous prisms, m. p. 232°. The crystalline *platinichloride* has m. p. 223°. E. F. A.

Synthesis of Betonidine and Turicine. ALBERT KÜNG (*Zeitsch. physiol. Chem.*, 1913, 85, 217—224. Compare preceding abstract).— γ -Hydroxyproline prepared by E. Fischer's method from gelatin can be methylated by means of potassium hydroxide in methyl alcohol and methyl iodide. The product, hydroxyprolinebetaine,



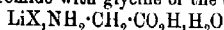
is a mixture of betonidine and turicine in equal quantities. The nature of the isomerism between these two betaines has not been established.

E. F. A.

Compounds of Hexamethylenetetramine with Various Silver Salts. LUDWIG VANINO and PAULA SACHS (*Arch. Pharm.*, 1913, 251, 290—293. Compare Grützner, A., 1899, i, 6).—The authors have prepared the compound of hexamethylenetetramine with silver nitrate, obtained by Grützner (*loc. cit.*), and also compounds with the following silver salts: silver fluoride, $\text{C}_6\text{H}_{12}\text{N}_4\cdot\text{AgF}\cdot 3\text{H}_2\text{O}$, slender needles; silver chloride, B_4AgCl , prismatic crystals (compare Délepine, A., 1895, i, 261); silver bromide, B_3AgBr , microscopic crystals; silver iodide, B_3AgI , amorphous; silver chlorate, $\text{B}_4\text{AgClO}_3\cdot\text{H}_2\text{O}$, amorphous, explodes on warming; silver oxalate, $\text{B}_4\text{Ag}_2\text{C}_2\text{O}_4$; globular masses of slender needles. T. A. H.

The Methylation of Glycine by means of Formaldehyde. WALTHER LÖB (*Biochem. Zeitsch.*, 1913, 51, 116—127).—If formaldehyde is allowed to act on glycine in neutral solution in the cold, a compound, $\text{CH}_2\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is formed, with separation of the elements of water, which under the influence of acids or alkalis readily undergoes scission again into formaldehyde and glycine. If, however, the substances are allowed to act on one another in hot acid solution, a stable *methylenediglycine*, $\text{CH}_2(\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, is formed, which can be readily isolated in the form of a dihydrochloride, from which, by means of silver oxide, the free base can be obtained in platelets, melting about 199°. In alkaline solution, formaldehyde does not act on glycine. If formaldehyde in the presence of acid and zinc is allowed to act on glycine (at 100°), a mixture of sarcosine and dimethylaminoacetic acid is produced. The mechanism of this reaction is explained by assuming that methylenediglycine is reduced to a mixture of an equal number of molecules of methylglycine and glycine. By the action of formaldehyde on the former, methylenedi(methylglycine) can be produced, which, on reduction, yields an equal number of molecules of dimethyl- and monomethyl-glycines. S. B. S.

Behaviour of α -Amino-acids and Polypeptides to Neutral Salts. PAUL PFEIFFER and J. VON MODELSKI (*Zeitsch. physiol. Chem.*, 1913, 85, 1—34. Compare A., 1912, i, 949).—The compounds of lithium chloride or bromide with glycine of the composition



are readily prepared by evaporating an aqueous solution of the components until crystallisation begins. They form colourless needles, m. p. 136° (the chloride) and $175-176^{\circ}$ (the bromide) respectively.

The compounds of the type $\text{LiX} \cdot 2\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \cdot \text{H}_2\text{O}$ are obtained by crystallising rapidly at room temperature from strong solutions after inoculation. They crystallise in colourless, transparent plates, m. p. $186-190^{\circ}$ (the chloride) and 223° (the bromide).

The compound of lithium chloride and alanine,
 $\text{LiCl} \cdot \text{NH}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{H} \cdot \text{H}_2\text{O}$,

has m. p. $128-129^{\circ}$.

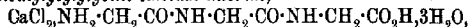
Monoglycine calcium chloride, $\text{CaCl}_2 \cdot \text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \cdot 3\text{H}_2\text{O}$, forms tiny, lustrous plates, which do not melt. *Diglycine calcium chloride*, $4\text{H}_2\text{O}$, crystallises in long, colourless needles. *Triglycine calcium chloride* separates in lustrous, transparent platelets which do not melt at 250° . *Triglycine lanthanum chloride*,



forms colourless, transparent, prismatic needles.

Monoalanine lithium chloride, $\text{LiCl} \cdot \text{NH}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{H} \cdot \text{H}_2\text{O}$, crystallises in colourless, lustrous platelets, m. p. $127-128^{\circ}$. *Dialanine calcium chloride*, $3\text{H}_2\text{O}$, yields colourless, transparent needles, m. p. 77° to a viscid, clear liquid.

Monodiglycylglycine calcium chloride,



separates in well-formed, colourless, transparent platelets.

Monobetaine potassium bromide, $\text{KBr} \cdot \text{C}_6\text{H}_{11}\text{O}_2\text{N} \cdot 2\text{H}_2\text{O}$, crystallises in transparent, tabular plates, which soften completely at $90-93^{\circ}$, m. p. about 110° . *Monobetaine potassium iodide* forms long, thin, colourless plates consisting in part of parallel, intergrown, flat needles, which sinter at 100° , begin to melt at 115° , and form a clear liquid at 140° . *Dibetaine potassium iodide* $\text{KI} \cdot 2\text{C}_6\text{H}_{11}\text{O}_2\text{N} \cdot 2\text{H}_2\text{O}$, forms colourless, tabular crystals with oblique faces, m. p. 148° . *Monobetaine barium chloride*, $4\text{H}_2\text{O}$, crystallises in long, thin, colourless, prismatic needles. *Monobetaine barium bromide*, $4\text{H}_2\text{O}$, also separates in similar needles.

The constitution of the salts described is discussed; they are regarded as amphi-salts in which both the basic and acid groups of the amino-acid are neutralised.

E. F. A.

Methyl Derivatives of δ -Aminovaleric Acid and *d,l*-Ornithine.

EMIL FISCHER and MAX BERGMANN (*Annalen*, 1913, 398, 96-124).—By hydrolysis with hydrochloric acid, D 1-19, in a sealed tube in the water-bath, δ -*m*-nitrobenzoylamino- α -methylaminovaleric acid (A., 1909, i, 793) readily yields δ -amino- α -methylaminovaleric acid dihydrochloride, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NHMe}) \cdot \text{CO}_2\text{H} \cdot 2\text{HCl}$, m. p. $207-210^{\circ}$ (decomp., corr.), colourless plates or prisms, which forms a precipitate with phosphotungstic acid, but not with potassium bismuth iodide even in considerably concentrated solutions. From the dihydrochloride, the *picrate*, $\text{C}_6\text{H}_4\text{O}_2\text{N}_2 \cdot 2\text{C}_6\text{H}_3\text{O}_2\text{N}_3$, m. p. $205-206^{\circ}$ (decomp., corr.), and the *platinichloride*, $\text{C}_6\text{H}_4\text{O}_2\text{N}_2 \cdot \text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ (or $4\text{H}_2\text{O}$), decomp. 218° (corr.), when anhydrous, have been prepared.

By treating an aqueous solution of the dihydrochloride with silver

sulphate, removing the excess of silver by hydrochloric acid and the sulphuric acid by barium hydroxide, and evaporating the filtrate at 10—20 mm., all the operations being performed in an atmosphere of carbon dioxide, δ -amino- α -methylaminovaleric acid, m. p. 82—100°, is obtained as a crystalline mass. Its aqueous solution reacts strongly alkaline, precipitates ferric hydroxide, and dissolves precipitated copper hydroxide.

By hydrolysing *dl*-benzoylornithine with boiling hydrochloric acid (D 1.19) and treating the resulting *dl*-ornithine with 2*N*-sodium hydroxide and benzenesulphonyl chloride (3 mols.) at 46—48°, and acidifying, $\alpha\delta$ -dibenzenesulphonyldiaminovaleric acid (*dl*-dibenzenesulphonylornithine), $C_{17}H_{20}O_8N_2S_2H_2O$, m. p. 155—157° (corr., anhydrous), microscopic needles, is obtained. By treatment with 2*N*-sodium hydroxide and methyl iodide at 65°, it yields, after acidification, $\alpha\delta$ -dibenzenesulphonyldimethyldiaminovaleric acid,

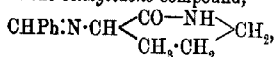
$SO_2Ph \cdot NMe \cdot CH_2 \cdot CH_2 \cdot CH(NMe \cdot SO_2Ph) \cdot CO_2H$, m. p. 141—142° (corr.), microscopic plates, by the hydrolysis of which by hydrochloric acid (D 1.19) at 100° is obtained *N*-dimethylornithine- $\alpha\delta$ -dimethyldiaminovaleric acid, $NHMe \cdot (CH_2)_3 \cdot CH(NHMe) \cdot CO_2H$, which is isolated by precipitation with phosphotungstic acid; the hydrochloride, $C_9H_{16}O_2N_2 \cdot 2HCl$, and *platinichloride*, $C_9H_{16}O_2N_2 \cdot H_4PtCl_6$, m. p. 220° (decomp., corr.), are described, and the *aureichloride* and *picrate* are mentioned. A 0.5% aqueous solution of dimethylornithine dihydrochloride and aqueous potassium bismuth iodide yield a brick-red precipitate after a few hours.

dl-Ornithine, obtained by the hydrolysis of δ -benzoylornithine, has been isolated in a crystalline state.

δ -Benzenesulphonylaminovaleric acid, 2*N*-sodium hydroxide, and methyl iodide at 63—65° yield, after acidification, δ -benzenesulphonylmethylaminovaleric acid, $SO_2Ph \cdot NMe \cdot (CH_2)_4 \cdot CO_2H$, m. p. 70—71° (corr.), colourless needles or prisms, by the hydrolysis of which by hydrochloric acid (D 1.19) is obtained δ -methylaminovaleric acid, m. p. 121—122° (corr.), needles or prisms, which is isolated by means of phosphotungstic acid. The acid is very hygroscopic, and its aqueous solution gives immediately a brick-red precipitate with potassium bismuth iodide; the *picrate*, $C_6H_{13}O_2N_2 \cdot C_6H_3O_7N_3 \cdot H_2O$, has m. p. 70—71° (corr.). At 130—160°, δ -methylaminovaleric acid loses water and is converted into

1-methyl-2-piperidone, $NMe \cdot \begin{matrix} CO-CH_2 \\ | \\ CH_2-CH_2 \end{matrix} > CH_2$, b. p. 94—95° (corr.)/9 mm.

3-Amino-2-piperidone, prepared from ornithine, reacts readily with benzaldehyde to form the *benzylidene* compound,



m. p. 140—143° (corr.), almost colourless crystals.

Glycine, *p*-toluenesulphonyl chloride, and 2*N*-sodium hydroxide at 67—70° yield, after acidification, *p*-toluenesulphonylglycine, $C_9H_{11}O_4NS$, m. p. 149—150° (corr.), slender needles, which is converted by 3*N*-sodium hydroxide and methyl iodide at 67° and subsequent

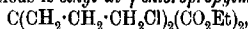
acidification into *p*-toluenesulphonylsarcosine, $C_{10}H_{13}O_2NS$, m. p. 150—152° (corr.), by the hydrolysis of which sarcosine is obtained.

The reaction of alcoholic sodium ethoxide, α -chloro- γ -bromopropene, and ethyl malonate in the presence of ether leads to the production of *ethyl γ -chloropropylmalonate*, $CH_2Cl \cdot CH_2 \cdot CH_2 \cdot CH(CO_2Et)_2$, b. p. 154—155° (corr.)/17 mm., which reacts with bromine in chloroform to form *ethyl bromo- γ -chloropropylmalonate*

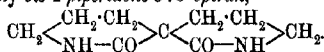


b. p. 175—176° (corr.)/17 mm. Ethyl γ -chloropropylmalonate and 33% aqueous methylamine react at the ordinary temperature to form *γ -chloropropylmalonmethylamide*, $CH_2Cl \cdot CH_2 \cdot CH_2 \cdot CH(CO \cdot NHMe)_2$, m. p. 158—162° (corr.), leaflets or needles.

A by-product in the preparation of ethyl γ -chloropropylmalonate under certain conditions is *ethyl di- γ -chloropropylmalonate*,



m. p. 51—52°, b. p. 195—197° (corr.)/14 mm., flattened crystals, which is converted by methyl alcoholic ammonia at 100° into a substance, $C_9H_{14}O_2N_2$, m. p. 330° (decomp., corr.), colourless, microscopic prisms, which is probably *bis-2-piperidone-3:3'-spiran*,



C. S.

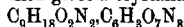
The Oxidative Degradation of a Synthetic Tripeptide. OTTO EISLER (*Biochem. Zeitsch.*, 1913, 51, 45—52).—By the oxidation of alanylglycylglycine with calcium permanganate, using as much of the latter as is equivalent to 8—10 atoms of oxygen to one molecule of the peptide, an acid in the form of a crystalline calcium salt was isolated, the formula of which corresponded approximately with



On hydrolysis by acids, one molecule gives rise to two molecules of oxalic acid. Two alternative formulæ are suggested by the author.

S. B. S.

Anhydride Formation with a Diaminohydroxy-acid. MORITZ KOHN and ALFONS OSTERSETZER (*Monatsh.*, 1913, 34, 781—786).—It has been shown (Kohn, A., 1908, i, 819; Kohn and Bum, A., 1910, i, 136) that isohexan- δ -ol- β -one on treatment with potassium cyanide and ammonium chloride, or the hydrochloride of an amine, gives rise to an aminolactone. When equimolecular quantities of isohexan- δ -ol- β -one, ethylenediamine dihydrochloride, potassium cyanide, and potassium hydroxide are heated together with a little water at 60° for five to six hours, and the resulting nitrile hydrolysed by treatment with concentrated hydrochloric acid, a substance, $C_9H_{18}O_2N_2$, prismatic crystals, m. p. 174°, is obtained, which gives a crystalline *picrate*,

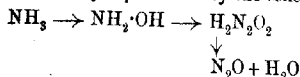


m. p. 154°, and an *oxalate*, $C_9H_{18}O_2N_2 \cdot 2C_2H_2O_4 \cdot \frac{1}{2}H_2O$, tablets, m. p. 160° (decomp.).

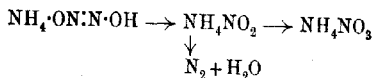
The structure of the substance is probably that of a diaminolactone or of a γ -hydroxylactam, but the point is at present undecided.

D. F. T.

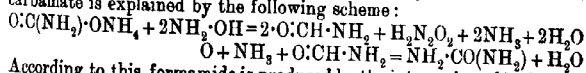
The Electrolytic Formation of Carbamide and Acetamidine Nitrate. FRITZ FICHTER, KARL STUTZ, and FRITZ GRIESHABER (*Verhandl. Naturforsch. Ges. Basel*, 1912, 23, 222—263).—It is shown that small quantities of carbamide are produced by the electrolysis of solutions of ammonium carbamate. The best yields, which are nevertheless very small, are obtained when the anode current density (C_a) lies between 0.130 and 0.555 ampere per sq. cm. Between these values the yield is practically constant and amounts to about 0.60 gram per 100 ampere-hours. It is shown that the yield is increased if the concentration of the carbamate is increased, and also increase of free ammonia increases the yield, the latter factor being of much more importance than the former. The best yield is obtained with a solution containing 12 gram-equivalents of ammonia and 8 gram-equivalents of ammonium carbamate. It is also shown that carbamide is decomposed by the oxidising action of the current and converted into ammonium nitrate, and that the amount of decomposition is greatest when there is no free ammonia present and that it decreases, rapidly as the concentration of ammonia is increased. The gases evolved at the anode were collected and analysed, and the relationship between their composition and the temperature and excess ammonia concentration determined. It is shown that at 18° with $C_a = 0.044$ ampere per sq. cm., the percentage of oxygen slowly decreases, whilst the nitrogen increases with the concentration of free ammonia up to 7 gram-equivalents per litre, and that on further increasing the free ammonia concentration the nitrogen increases rapidly until at 12 gram-equivalents per litre it has reached 100%. From a solution containing 9 gram-equivalents of ammonia the percentage of nitrogen in the gas was 24.8% at 6°, whilst at 18° it had increased to 99.1%. A theory is put forward to represent the electrolytic oxidation of ammonia which can be shortly represented by the scheme:



and

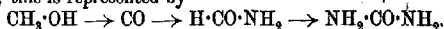


Nitrous oxide is found in the gases collected at the anode, and the other steps in the process are generally confirmed by the observations. The formation of carbamide by the electrolysis of ammonium carbamate is explained by the following scheme:

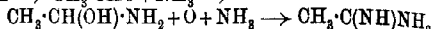
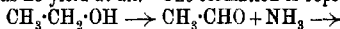


According to this, formamide is produced by the interaction of hydroxylamine, produced as above, and ammonium carbamate, and this is then electrolytically oxidised in the presence of ammonia to carbamide. In proof of this theory the authors quote the work of Jouve (A., 1899, i, 420), who showed that when carbon monoxide is heated with ammoniacal cuprous chloride, carbamide is produced. Further, Hofmeister and Halsey (A., 1898, ii, 529) have shown that a large number

of organic substances when treated with potassium permanganate in ammoniacal solution yield carbamide. These substances are all oxy-acids, ketones, and ketonic acids, that is, substances which give carbon monoxide on oxidation. Carbamide was next obtained by electrolysing a solution of ammonium acetate containing methyl alcohol; this is represented by



When ethyl alcohol was electrolysed in ammoniacal solution a small quantity of acetamidine nitrate was obtained. It was found that the addition of ammonium nitrate increased the yield of the amidine nitrate, and that if no ammonium nitrate had been added, often there was no yield at all. The formation is represented by the scheme:



The authors show in confirmation of the above that aldehyde ammonia can be oxidised to the amidine by calcium permanganate, ammonium per-sulphate and hydrogen peroxide, and isolated provided that excess of ammonia and some ammonium nitrate are present. The corresponding propionamidine nitrate and butyramidine nitrate were obtained by the electrolysis of ammoniacal solutions of propyl and butyl alcohols respectively. In the case of butyl alcohol only the smallest yield was obtained, and with higher alcohols amidine nitrates could not be obtained in any case.

J. F. S.

The Fixation of Nitrogen by Mixtures of Barium Oxide and Charcoal. THOMAS EWAN and THOMAS NAPIER (*J. Soc. Chem. Ind.*, 1913, 32, 467—474).—The first set of experiments were carried out by heating a mixture of two parts of barium carbonate and one part of well-burned wood charcoal, contained in an iron boat, in a porcelain tube is a current of nitrogen. The results obtained were as follows (compare Kühling and Berkhold, A., 1908, i, 143): the absorption of nitrogen begins between 900° and 930°. The amount absorbed under the same conditions increases very rapidly with the temperature, for example, if 4 mols. of nitrogen are passed over 1 mol. of BaCO_3 in two hours, about 1% of the barium will combine with it at 930°, about 14% at 960°, and about 40% at 1000°. The greater part of the nitrogen fixed is in the form of cyanide. Under the conditions used by the authors, about 2.5% of the nitrogen used is fixed at 960° and about 10% at 1000°. The addition of quantities of potassium carbonate up to 11% seems to improve the results, but the improvement is no more than would be produced by a difference of 10—20° in temperature.

No cyanide is formed until some 30% of the barium carbonate has been converted into oxide, and the quantity of carbon monoxide in the gas has fallen to about 30%; the percentage of carbon monoxide falls steadily as the formation of cyanide progresses.

The authors draw the conclusion that the fixation of nitrogen is due to one or both of the reversible reactions: $\text{BaO} + 2\text{C} + \text{N}_2 \rightleftharpoons \text{BaCN}_2 + \text{CO}$, $\text{BaO} + 3\text{C} + \text{N}_2 \rightleftharpoons \text{Ba}(\text{CN})_2 + \text{CO}$; and further experiments indicate that the barium compounds mix in the solid (or fused) mixture, so that the ratio of the partial pressures of carbon monoxide and nitrogen in

the gas when equilibrium is attained at any given temperature depends on the relative quantities of cyanide, cyanamide, and oxide in the mixture. The reaction appears to be arrested at half-conversion of the barium oxide, which may be explained by assuming the formation of a compound $\text{BaO} \cdot \text{Ba}(\text{CN})_2$, in which the barium oxide is much less active than in the free state.

Pure barium cyanide is readily obtained by suspending anhydrous barium hydroxide, in the form of a fine powder, in light petroleum, and adding an emulsion of the theoretical quantity of anhydrous hydrocyanic acid in light petroleum. It fuses at 600° and is distinctly volatile even at its melting point. The fused product contains barium cyanamide, the amount of which depends, among other things, on the temperature and the length of time the fusion is heated; the presence of finely divided iron in the cyanide increases the amount of cyanamide formed.

When barium ferrocyanide is heated in a vacuum or in an atmosphere of nitrogen, decomposition begins at about 500° , nitrogen is evolved, and a mixture of carbon, iron, and barium cyanide and cyanamide remains behind.

When mixtures of barium oxide, cyanide, and cyanamide are heated in nitrogen, the combined nitrogen passes more and more into the form of cyanide as the mixture is more and more diluted with barium oxide.

T. S. P.

Some Aliphatic Cyanoacetylaminos. MARIA CLOTILDE BIANCHI (*Atti R. Accad. Sci. Torino*, 1912-1913, 48, 654-659).—*Cyanoacetomethylamide*, $\text{CN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHMe}$, is prepared with almost the theoretical yield by passing gaseous methylamine into an alcoholic solution of ethyl cyanoacetate; it crystallises in prisms, m. p. about $104-105^\circ$. *Cyanoacetoethylamide*, $\text{CN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHEt}$, is similarly prepared and forms prismatic laminæ, m. p. $74-75^\circ$; it is oxidised by potassium permanganate at the ordinary temperature.

Dicyanoacetopropylenediamide, $(\text{CN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH})_2 \text{C}_3\text{H}_6$, obtained by keeping a mixture of ethyl cyanoacetate and propylenediamine for twenty-four hours, crystallises in colourless needles, m. p. $161-162^\circ$.

Dicyanoacetotrimethylenediamide, $\text{CH}_2(\text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CN})_2$, prepared by mixing ethyl cyanoacetate and trimethylenediamine, crystallises in slightly yellow needles, m. p. $163-165^\circ$.

Cyanoacetamide, after recrystallisation from ether, has m. p. $124-125^\circ$, which is higher than the m. p. given in the literature.

R. V. S.

Photochemical Synthesis of a New Compound, Carbonyl Cyanide, by means of Ultra-violet Rays. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, 156, 1766-1768).—Carbon monoxide and cyanogen when mixed and subjected to the ultra-violet rays ($\lambda < 0.25 \mu$) from a mercury-quartz lamp combine to form *carbonyl cyanide*, $\text{CO}(\text{CN})_2$, a yellow, amorphous compound, which does not volatilise at 200° , but gives off small quantities of nitrogen. It is soluble in alkalis, giving a yellow solution, and slowly

undergoes hydrolysis on the addition of acid, giving carbon dioxide and hydrogen cyanide. It burns only very slowly in oxygen at a red heat.
W. G.

[Potassium Manganicyanide.] JULIUS MEYER (*Zeitsch. anorg. Chem.*, 1913, 81, 385—405).—See this vol., ii, 599.

Some Azides of Carbamic Acid. VI. E. OLIVERI-MANDALA and F. NORO (*Gazzetta*, 1913, 43, i, 514—520).—The azides described in this paper were prepared by the action of azoimide on carbimides. Methylcarbamazide can be obtained in this way. *Chloromethylcarbamazide* (from chloromethylcarbimide in benzene solution) decomposes rapidly on exposure to the air. Alcoholic ammonia converts it into a substance, $(C_2H_5ON_2Cl)_3$, having the composition of a *trimeride* of the *chloromethylcarbamide* to be expected; it decomposes above 300° , evolving hydrogen chloride.

Bromomethylcarbamazide is similarly obtained from *bromomethylcarbimide*, which can be prepared by Schroeter's method (A., 1909, i, 773); this azide is also very unstable. When it is treated with alcoholic ammonia, a *trimeric bromomethylcarbamide*, $(C_2H_5ON_2Br)_3$, is produced; it decomposes above 300° .

Propylcarbimide, prepared from silver cyanate and propyl iodide, has b. p. $82-85^\circ$. The *azide*, $C_4H_9ON_3$, has b. p. $85-86^\circ/28$ mm. When heated for two hours with aniline in alcoholic solution, it yields *s-phenylpropylcarbamide*, $C_{10}H_{14}ON_2$, m. p. $114-116^\circ$.

isoPropylcarbamazide, $C_4H_9ON_3$, crystallises in long needles, m. p. 44° . *s-Phenylisopropylcarbamide*, $C_{10}H_{14}ON_2$, obtained from this azide, forms needles, m. p. $142-143^\circ$.

isoButylcarbamazide, $C_5H_{10}ON_3$, has b. p. $94^\circ/22$ mm. *s-Phenylisobutylcarbamide*, $C_{11}H_{16}ON_2$, crystallises in small needles, m. p. 158° .

R. V. S.

A New Class of Lipoid Arsenic Compounds. EMIL FISCHER and GEORG KLEMPFNER (*Therapie der Gegenwart*, Jan., 1913; Reprint 8 pp.).—When behenic acid is heated with arsenic trichloride and the product of action is afterwards treated with bases, an acid containing arsenic and chlorine in approximately equivalent quantities is formed. It has been obtained so far as a coloured oil, which is not sufficiently pure for analysis. The strontium salt, containing about 13% arsenic and 6% chlorine, has been employed under the name of *elarsen* as a medicament containing arsenic in a relatively non-toxic form, and satisfactory therapeutic results are claimed for it in cases requiring treatment by arsenic.
S. B. S.

Hydro-aromatic Substances. ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Rep. Brit. Assoc.*, 1912, 124—125).—See Crossley and Renouf, T., 1912, 101, 1524; Crossley and Smith, P., 1912, 332.
C. H. D.

Preparation of Several Dicyclohexylbutanes. PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1913, 156, 1430—1434. Compare A., 1912, i, 547, 617, 757).—By direct hydrogenation with reduced

nickel the authors have prepared five of the nine possible dicyclohexylbutanes, three being derivatives of *n*-butane and two of *iso*-butane; $\alpha\delta$ -dicyclohexylbutane, $C_6H_{11}[(CH_2)_4C_6H_{11}]_2$, colourless crystals, m. p. 9° , b. p. $304\text{--}306^\circ$ (corr.), D_4^{20} 0.8772, n_D^{20} 1.475, is obtained by the reduction of $\alpha\delta$ -diphenylbutane.

Phenyl ethyl ketone reacts with magnesium benzyl chloride at 450° in the presence of thorium oxide to give phenylbenzylethylcarbinol, which by distillation under reduced pressure yields diphenyl- Δ^a -butylene, b. p. 296° (corr.), D_4^{18} 1.0124, n_D^{18} 1.593 (compare Klages and Heilmann, A., 1904, i, 487). This hydrocarbon on hydrogenation in the presence of slightly active nickel gives $\alpha\beta$ -diphenylbutane, a colourless liquid, b. p. $285\text{--}287^\circ$ (corr.), D_4^{18} 1.0092, n_D^{18} 1.587, which on further hydrogenation over very active nickel at 170° yields $\alpha\beta$ -dicyclohexylbutane, a colourless liquid, b. p. $276\text{--}278^\circ$ (corr.), D_4^{20} 0.9104, D_4^{18} 0.9084, n_D^{18} 1.500.

$\alpha\alpha$ -Diphenyl- Δ^a -butylene, b. p. $295\text{--}297^\circ$ (corr.), D_4^{18} 1.0039, n_D^{18} 1.595, obtained by the interaction of magnesium phenyl bromide and ethyl butyrate and subsequent dehydration, on hydrogenation at 150° with slightly active nickel yields $\alpha\alpha$ -diphenylbutane, b. p. $286\text{--}288^\circ$ (corr.), D_4^{18} 0.9748, n_D^{18} 1.554. If this hydrogenation is carried out at 250° the product is diphenylmethane, m. p. 27° , b. p. 262° , described by Klages and Heilmann (*loc. cit.*) as $\alpha\alpha$ -diphenylbutane. The $\alpha\alpha$ -diphenylbutane, now described, on hydrogenation at 170° with very active nickel yields $\alpha\alpha$ -dicyclohexylbutane, b. p. $280\text{--}282^\circ$ (corr.), D_4^{20} 0.8922, D_4^{18} 0.8842, n_D^{18} 1.485.

By the interaction of benzophenone and magnesium isopropyl iodide or by the action of magnesium phenyl bromide on ethyl isobutyrate, and subsequent dehydration of the carbinol formed, $\alpha\alpha$ -diphenyl- β -methylpropylene, b. p. 293° , D_4^{16} 1.0240, n_D^{16} 1.596, is obtained, and this on gentle hydrogenation at 180° yields $\alpha\alpha$ -diphenyl- β -methylpropane, b. p. $285\text{--}286^\circ$ (corr.), D_4^{16} 0.978, n_D^{16} 1.560. This hydrocarbon by more active hydrogenation at 170° gives $\alpha\alpha$ -dicyclohexyl- β -methylpropane, b. p. $278\text{--}279^\circ$ (corr.), D_4^{16} 0.9017, D_4^{15} 0.8906, n_D^{15} 1.492.

$\alpha\gamma$ -Diphenyl- β -methylpropylene, b. p. 304° (corr.), D_4^{16} 1.0181, n_D^{16} 1.593, obtained in the usual way from magnesium methyl iodide and dibenzyl ketone, on hydrogenation at 170° with very active nickel yields $\alpha\gamma$ -dicyclohexyl- β -methylpropane, b. p. $290\text{--}292^\circ$ (corr.), D_4^{16} 0.8916, D_4^{15} 0.8840, n_D^{15} 1.484.

W. G.

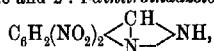
Partial Reduction of Aromatic Polynitro-compounds by Electrochemical Methods. III. KURT BRAND and TH. EISENMENGER (*J. pr. Chem.*, 1913, [ii], 87, 487—507. Compare A., 1906, i, 80; 1907, i, 755).—The present paper deals with the electrolytic reduction of 2:4:6-trinitrotoluene, 2:4-dinitroanisole, and 4-chloro-*m*-dinitrobenzene in alkaline, acid and almost neutral solution.

On reduction in alkaline solution at a mercury cathode, 4-chloro-*m*-dinitrobenzene yields 4-chloro-*m*-nitroaniline and 6-chloro-*m*-nitroaniline, together with 2:4-dinitrophenol; under the same conditions, 2:4-dinitroanisole is reduced to 5:5'-dinitro-*o*-azoxyanisole, which separates from benzene in slender, almost colourless leaflets, m. p. 209° .

The constitution of the azoxy-compound has been established by its

preparation from 5-nitro-2-methoxyphenylhydroxylamine by the action of sodium hydroxide in alcoholic solution. The reduction of 2:4:6-trinitrotoluene in alkaline solution yielded no definite product. In hydrochloric acid solution and in the presence of cupric chloride, 2:4:6-trinitrotoluene is reduced at a copper cathode to 2:6-dinitro-*p*-toluidine and 4:6-dinitro-*o*-toluidine.

The last-named compound forms orange-yellow crystals, which have m. p. 135° and not 155° as given by Holleman and Böeseken (A., 1898, i, 303). It yields an *acetyl* derivative, crystallises in white needles, m. p. 224°, and when diazotised and boiled with alcohol is converted into 2:4-dinitrotoluene and 2:4-dinitroindazole,



which crystallises in almost white needles, m. p. 203°, and dissolves in aqueous alkalis, yielding yellow solutions.

On reduction in acid solution under the same conditions as given above for 2:4:6-trinitrotoluene, 2:4-dinitroanisole yields 4-nitro-*o*-anisidine (Meldola, Woolcott, and Wray, T., 1896, 69, 1321), whilst 4-chloro-*m*-dinitrobenzene gives rise to 4-chloro-*m*-nitroaniline and 6-chloro-*m*-nitroaniline, which are separated by crystallisation of their *acetyl* derivatives from alcohol.

In almost neutral solution, 2:4:6-trinitrotoluene is reduced at a silver cathode to 2:6-dinitro-*p*-tolylhydroxylamine (Cohen and Dakin, T., 1902, 81, 27) and 4:6-dinitro-*o*-tolylhydroxylamine, which forms light yellow crystals, m. p. 109°.

The constitution of 2:6-dinitro-*p*-tolylhydroxylamine has been confirmed by its reduction with copper powder and hydrochloric acid to 2:6-dinitro-*p*-toluidine, and conversion of the latter compound by diazotisation and boiling with alcohol into 2:6-dinitrotoluene. When boiled with strong hydrochloric acid, 2:6-dinitro-*p*-tolylhydroxylamine yields 3:5:3':5'-tetranitro-*p*-azoxytoluene, colourless needles, m. p. 216°; on treatment with phosphorus pentachloride in ethereal solution it gives rise to 3:5:3':5'-tetranitro-*p*-azotoluene, which crystallises in orange needles, m. p. 248—250°.

Reduction of 4-chloro-*m*-dinitrobenzene in almost neutral solution yields a small amount of 2:2'(or 4:4')-dichloro-5:5'-dinitroazobenzene, m. p. 164°, together with a brown oil, containing 4- and 6-chloro-*m*-nitrophenylhydroxylamines, which, however, could not be isolated from the product, and were therefore identified by oxidation of the cathode liquid with ferric chloride to the corresponding nitroso-compounds.

1-Chloro-4-nitro-2-nitrosobenzene forms white needles, m. p. 95°, and has also been prepared by the oxidation of 6-chloro-*m*-nitroaniline with Caro's acid.

1-Chloro-2-nitro-4-nitrosobenzene, prepared from 4-chloro-*m*-nitroaniline in a similar manner, forms white needles, m. p. 120°.

In neutral solution, 2:4-dinitroanisole is reduced at a silver cathode to the above-mentioned 5:5'-dinitro-*o*-azoxyanisole and 5-nitro-2-methoxyphenylhydroxylamine, which forms a brownish-red, sandy, crystalline powder, m. p. 129°, is reduced by copper powder and hydrochloric acid to 4-nitro-*o*-anisidine, and on oxidation with ferric chloride yields a

compound, $C_{16}H_{16}O_8N_4$, m. p. 121° , the constitution of which has not yet been determined.

F. B.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. FREDERICK S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, and JOHN T. HEWITT (*Rep. Brit. Assoc.*, 1912, 118—123).—See Orton and Jones, T., 1912, 101, 1708, 1720.

C. H. D.

A Photochemical Reaction. FRÉDÉRIC REVERDIN (*Bull. Soc. chim.*, 1913, [iv], 13, 485—486 *).—A solution of 3:5-dinitro-4-nitromethylaminotoluene in alcohol on exposure to sunlight slowly undergoes partial transformation into 3:5-dinitro-4-methylaminotoluene.

T. A. H.

Hexylenic Ethers. R. DIONNEAU (*Bull. Soc. chim.*, 1913, [iv], 13, 519—525).—A more detailed account, with some new data, of work already recorded (A., 1910, i, 353). Phenoxyhexylene, D_4^0 0.9553, reacts with bromine in chloroform to give a *dibromide*, D_4^1 1.5415, b. p. $208^\circ/35$ mm. (decomp.), and with excess of hydriodic acid to form di-iodohexane, D_4^0 2.047, whilst with 1 mol. of the acid it gives iodophenoxyhexane, D_4^1 1.4385, b. p. $205^\circ/33$ mm., and a *substance*, D_4^1 1.516, b. p. $84^\circ/33$ mm. or $183^\circ/760$ mm., which may be iodo-hexylene. Iodophenoxyhexane through its magnesium derivative yields phenoxyhexane, from which Francbimont and Zincke's hexyl iodide is obtainable by heating with hydriodic acid; thus showing that in phenoxyhexylene the radicle C_6H_{11} is linear and carries the phenoxy-group on the first carbon atom. On oxidation with permanganate or ozone, phenoxyhexylene yields phenoxyvaleric and formic acids. These observations indicate that it has the formula $OPh\cdot[CH_2]_4\cdot CH:CH_2$.

Ethoxyhexylene (*loc. cit.*) has been prepared by the action of allyl iodide on the magnesium derivative of iodoethoxypropane.

T. A. H.

Aliphatic Dihalogen Compounds. JULIUS VON BRAUN (*Ber.*, 1913, 46, 1782—1792).—A series of experiments is described on (1) the synthesis of brominated esters, (2) the preparation of polymethylene dibromides in which one $-CH_2-$ group is replaced by $-N(CN)-$, (3) ring-formations with sodium cyanamide, and (4) certain other ring-formations.

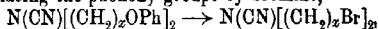
(1) Diprimary chloro-, bromo-, and iodo-compounds react readily with alkali phenoxides and alkoxides with the formation of halogenated ethers (for example, $Br[CH_2]_x\cdot OPh$), the use of which in synthetic operations is greatly limited by the difficulty of removing the phenoxy-radicle without completely decomposing the molecule. The author has, therefore, examined the halogen derivatives of alkyl carboxylates (compare A., 1909, i, 419) in this respect. When dry sodium benzoate (1 mol.) is heated with 1.5 mols. of various dibromides, the nature of the product formed depends greatly on the distance of the bromine atoms

* and *J. pr. Chem.*, 1913, [ii], 88, 90—91.

from one another. Ethylene dibromide yields almost exclusively ethylene dibenzoate, bromoethyl benzoate, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{O}\cdot\text{COPh}$, not being detectable; in the trimethylene series, the yield of brominated ester is 30%, in the tetramethylene series 45%, in the pentamethylene series above 60%, and in the heptamethylene series nearly 75%. These esters are readily saponifiable by acid or alkali, or even by protracted action of water and alcohol.

Trimethylene bromide and sodium benzoate yield trimethylene dibenzoate, m. p. 57° , and γ -bromopropyl benzoate, b. p. $162\text{--}164^\circ/14$ mm. When warmed with sodium iodide in alcoholic solution, the latter yields γ -iodopropyl benzoate, pale yellow oil, b. p. $175\text{--}178^\circ/12$ mm. δ -Bromobutyl benzoate, b. p. $176\text{--}178^\circ/14$ mm., together with tetramethylene dibenzoate, is similarly obtained from tetramethylene bromide. ϵ -Bromoamyl benzoate, b. p. $188\text{--}190^\circ/12$ mm., is most readily obtained from α : ϵ -dibromopentane and sodium benzoate at $200\text{--}210^\circ$. The corresponding pentamethylene dibenzoate is a liquid. ϵ -Bromoamyl benzoate is readily saponified by aqueous alcoholic potassium hydroxide with formation of pentamethylene oxide (compare Clarke, T., 1913, 101, 1802). η -Bromoheptyl benzoate is an oil, b. p. $205\text{--}210^\circ/11$ mm., which does not solidify. With sodium iodide it yields η -iodoheptyl benzoate, pale yellow oil, b. p. $220\text{--}224^\circ/11$ mm.

(2) The observation that in phenoxypropylbromoamylcyanamide (A., 1909, i, 507) the phenoxy-group is replaced by bromine more readily than the nitrile group is saponified under the action of hydrobromic acid has led the author to examine the possibility of introducing two phenoxy-alkyl residues into sodium cyanamide (compare Traube and Engelhardt, A., 1911, i, 955) with the ultimate object of replacing the phenoxy-groups by bromine,



and thus obtaining polymethylene dibromides in which one $\text{-CH}_2\text{-}$ group is replaced by $\text{CN}\cdot\text{N}<$.

γ -Phenoxypropyl iodide in alcoholic solution reacts readily with commercial sodium cyanide, yielding allyl phenyl ether and *diphenoxypropylcyanamide*, b. p. $295\text{--}300^\circ/13$ mm. The yield of the latter is nearly 60% of that theoretically possible. Fuming hydrobromic acid converts it into *dibromopropylcyanamide*, $\text{CN}\cdot\text{N}[(\text{CH}_2)_3\cdot\text{Br}]_2$, a pale brown, heavy oil which is not volatile with steam, and cannot be distilled without decomposition. When dissolved in dry ether, it reacts readily with metallic sodium, yielding a product which is only partly volatile in a vacuum. The volatile portion, b. p. $110\text{--}120^\circ/11$ mm., was hydrolysed with hydrochloric acid, and identified as hexamethyleneimine; the non-volatile portion was not identified. Phenoxyethyl bromide scarcely reacts with sodium cyanamide, but the corresponding iodide, m. p. $31\text{--}32^\circ$, yields phenylvinyl ether and *diphenoxyethylcyanamide*, white leaflets, m. p. 96° . In this compound the cyano- and phenoxy-groups are more simultaneously affected by hydrobromic acid than is the case with *diphenoxypropylcyanamide*, so that an approximately pure *dibromide* could only be obtained in small quantity. From β -iodoethyl ethyl ether, $\text{I}\cdot[\text{CH}_2]_3\cdot\text{O}\cdot\text{C}_2\text{H}_5$, and sodium cyanamide, the corresponding unsaturated ether is produced, whilst

ϵ -iodoamyl phenyl ether gives a product which is decomposed during distillation into amylene phenyl ether, $\text{CH}_3\cdot\text{CH}(\text{CH}_2)_3\cdot\text{OPh}$.

(3) When sodium cyanamide is boiled with an alcoholic solution of α : ϵ -pentamethylene dibromide, and the product treated with water, an oil is obtained which below $100^\circ/12$ mm. yields a small unsaturated fraction, at $110^\circ/12$ mm. gives a trace of 1-cyanopiperidine, and leaves a viscous, non-volatile oil. Similar results are obtained with α : ϵ -diiodopentane and α : δ -diiodobutane. From *o*-xylylene bromide and sodium cyanamide, a viscous product is obtained from which a small amount of a crystalline product, m. p. $235-236^\circ$, can be separated by methyl alcohol; the substance appears to be a polymeride of cyanodihydroisindole.

(4) α : γ -Dibromoheptane forms with ethyl sodioacetacetate an oil, which is decomposed on distillation, and on saponification yields β : μ -diketotridecane, $\text{COMe}\cdot[\text{CH}_2]_9\cdot\text{COMe}$, m. p. 72° (*semicarbazone*, m. p. 184°), together with nonanedicarboxylic acid and small quantities of the *keto-acid*, $\text{COMe}\cdot[\text{CH}_2]_9\cdot\text{CO}_2\text{H}$, m. p. $59-62^\circ$. The latter was not obtained in the pure state.

An attempt was made to synthesise suberone from α : δ -dibromobutane and ethyl acetonedicarboxylate. The desired substance was only obtained in very small quantity.

Attempts were further made to form cyclic compounds containing mercury, by the action of sodium amalgam on α : δ -diiodobutane and α : ϵ -diiodopentane respectively. The substances obtained were only partly volatile in a vacuum, and probably consisted of polymerides of the substances required.

H. W.

Amino-alcohols. Derivatives of Phenyl Glyceryl Ethers.

P. BRENNANS (*Bull. Soc. chim.*, 1913, [iv], 13, 525-535).—In continuation of the work of Fournéau (A., 1910, i, 246, 822), a number of new amino-alcohols of these types have been prepared with a view to the investigation of their therapeutic properties.

o-Nitrophenoxypropanediol, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, m. p. 45° , results from the action of monochlorohydrin on *o*-nitrophenol in presence of potassium hydroxide; it crystallises in yellow spangles, and on reduction with tin and hydrochloric acid yields *o*-aminophenoxypropanediol hydrochloride, m. p. 170° , crystallising in silky needles; the free base is very soluble in water. *o*-Nitrophenyl glycidic ether, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$, m. p. $51-52^\circ$, formed by the action of

dichlorohydrin on *o*-nitrophenol in presence of alkali, crystallises in pale yellow needles. In this reaction some dinitrodiphenoxypropanol, m. p. 122° (compare Fournéau, *loc. cit.*), is formed.

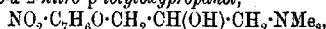
p-Nitrophenoxypropanediol, m. p. 58° , prepared by the general method (above and *loc. cit.*), crystallises in slender, colourless needles, and on reduction furnishes the corresponding amino-compound, m. p. 133° , crystallising in ragged tablets and becoming brown in the light; the hydrochloride, m. p. 166° , forms colourless scales.

Tetranitrodiphenoxypropanol, $\text{OH}\cdot\text{CH}[\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2]_2$, m. p.

79°, obtained by the action of epichlorohydrin on the potassium derivative of 2:4-dinitrophenol, in presence of excess of alkali, or, better, on the silver derivative of the phenol, forms large, yellow, tinted crystals. On reduction with tin and hydrochloric acid, it yields the corresponding *tetra-amino-compound hydrochloride*, crystallising from methyl alcohol in small, yellow prisms and decomposing below 200° when heated.

o-Nitro-p-tolyl glycidic ether, $\text{NO}_2 \cdot \text{C}_7\text{H}_4\text{O} \cdot \text{CH}_2 \cdot \text{CH} \begin{array}{c} \text{CH}_2 \\ \diagup \diagdown \\ \text{O} \end{array}$, m. p.

66—67°, prepared by the action of dichlorohydrin on 2-nitro-*p*-cresol in presence of alkali, crystallises in bright yellow prisms. When heated with dimethylamine at 100° during ten hours, it yields *γ-dimethylamino-α-2-nitro-p-tolxyloxypropanol*,



as a thick, yellow oil, giving a crystalline *benzoyl* derivative, m. p. 179°.

o-Iodophenoxypropanediol, m. p. 95°, prepared from *o*-iodophenol by the general method, crystallises in silky, colourless needles. *o-Iodo-phenyl glycidic ether*, b. p. 200—202°/20 mm., is a colourless liquid, which, with dimethylamine, yields *γ-dimethylamino-α-o-iodophenoxypropanol*, b. p. 210°/20 mm. (decomp.), as a colourless syrup from which the *benzoylated hydrochloride*, m. p. 169—170°, may be obtained as slender, prismatic needles.

5-Iodoguanacyloxypropanediol, $\text{OMe} \cdot \text{C}_5\text{H}_2\text{I} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, m. p. 109°, crystallises in slender, colourless, odourless needles.

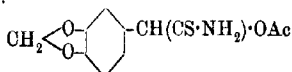
γ-Dimethylamino-α-o-tolxyloxypropanol, b. p. 175—178°/28 mm., gives a *benzoyl* derivative, the *hydrochloride* of which has m. p. 138° and crystallises in colourless, silky needles.

p-Nitrobenzoyl-γ-dimethylamino-α-thymoxypropanol hydrochloride, m. p. 161°, crystallises in large, yellow, octahedra from a mixture of alcohol and ether; the *meta-isomeride*, m. p. 187°, forms small, hard prisms from alcohol.

m-Tolyl glycidic ether, b. p. 136.5°/14 mm., on treatment with dimethylamine gives *γ-dimethylamino-α-m-tolxyloxypropanol*, b. p. 178—180°/14 mm., as a colourless syrup; the *benzoylated hydrochloride*, m. p. 138—139°, crystallises in rectangular tablets from acetone.

T. A. H.

Preparation of Derivatives of Aldehyde- and Keto-cyano-hydrins containing Sulphur.

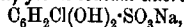


AUGUST ALBERT (D.R.-P. 259502).

—The crystalline compound (annexed formula), decomp. 145°, is obtained when a benzene solution of methylenedioxyacetylmandelonitrile, $\text{CH}_2 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_5 \cdot \text{CH}(\text{CN}) \cdot \text{OAc}$, is treated with alcoholic ammonia and the solution saturated at 0° with hydrogen sulphide; after some time the product separates in crystalline form.

The compound from benzoyl-*o*-nitromandelonitrile crystallises with 1 mol. of ethyl alcohol and decomposes at 160°. F. M. G. M.

Chloroquinolsulphonic Acids and Their Conversion into Chloro-*p*-benzoquinonesulphonic Acids. ALPHONSE SEYEWETZ and J. PARIS (*Bull. Soc. chim.*, 1913, [iv], 13, 486—491. Compare A., 1911, i, 360; this vol., i, 492).—Part of this work has been described already (*loc. cit.*). Chloroquinol on sulphonation by the method already described (*loc. cit.*) yields *sodium chloroquinolsulphonate*,



colourless leaflets, soluble in water, but not in alcohol, which acts as a photographic developer in presence of alkalis, and on oxidation by sodium dichromate and sulphuric acid yields *sodium chloro-*p*-benzoquinonesulphonate*, bright yellow needles, soluble in water but not in alcohol, which has oxidising properties, and in aqueous solution liberates iodine from iodides in presence of acids.

T. A. H.

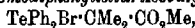
Unsaturated Compounds. Method of Reaction of Enols and Phenols. KURT H. MEYER and S. LENHARDT (*Annalen*, 1913, 398, 66—82).—It has been shown (this vol., i, 704) that the enolic grouping represents one of the most reactive states in organic chemistry. The additive capacity of the double linking is enormously increased by the presence of the hydroxyl group, as is proved by comparative experiments on the rate of addition, of alcoholic bromine and of *p*-nitrobenzenediazonium hydroxide, to pairs of substances differing only by the one containing a hydroxyl group where the other contains a hydrogen atom, as, for example, styryl methyl ketone and benzoyl-acetone. The reactivity of the enolic grouping is not connected, as Hinsberg supposes, with the dissociability of the hydrogen atom, because alkyl ethers of enols, which do not contain the mobile hydrogen atom, are also extremely reactive.

Recent researches on the action of ozone, potassium permanganate, and hydrogen on benzene have shown that the latter behaves like a substance containing very slowly reacting ethylenic linkings. The comparatively great reactivity of phenol, therefore, is explicable as being due to the activating influence of the hydroxyl group on the double linking. This view is supported by the fact that phenolic ethers are almost as reactive as phenol itself. Phenol, anisole, resorcinol, resorcinol dimethyl ether, α -naphthol, α -naphthyl methyl ether, β -naphthol, β -naphthyl methyl ether, and anthranol each reacts instantly with alcoholic bromine at 0°. The preceding ethers with the exception of anisole react as readily as phenol with diazo-hydroxides; *benzenaeazophloroglucinol trimethyl ether*, m. p. 82.5°, garnet-red crystals, easily soluble in dilute mineral acids, *p*-nitrobenzenaeazophloroglucinol trimethyl ether, m. p. 150.5°, brown needles with violet lustre, *p*-nitrobenzenaeazoresorcinyll dimethyl ether, m. p. 152°, red needles, and *p*-nitrobenzenaeazo- α -naphthyl methyl ether, m. p. 169°, red needles, are described. α -Naphthyl methyl ether in glacial acetic acid reacts readily with nitrous acid, yielding nitroso- α -naphthol, methyl alcohol being eliminated.

It is probable that all substances containing the groups $\cdot\text{CH}:\text{C}:\text{OR}$ or $\cdot\text{CH}:\text{C}:\text{NR}$ contain an activated ethylenic linking. Examples of the latter kind are found in the reactivity of pyrroles with aldehydes, halogens, and diazo-compounds; 1:2-dimethylindole condenses with

p-nitrobenzenediazonium hydroxide in glacial acetic acid to form a substance, $C_{16}H_{14}O_2N_4$, m. p. 204—205°, dark red crystals. C. S.

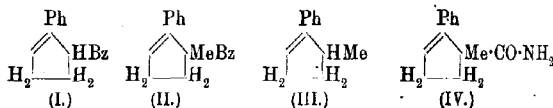
Aromatic Telluretine Compounds. II. KARL LEDERER (*Ber.*, 1913, 46, 1810—1812. Compare this vol., i, 615).—The methyl, ethyl, and propyl esters of α -bromopropionic acid have been heated to 50° with diphenyl telluride and the telluretine compounds isolated with difficulty and in poor yields. *Methyl diphenyl- α -propionyltelluretine bromide* [α -bromodiphenyltelluripropionate], $TePh_2Br\cdot CHMe\cdot CO_2Me$, and the ethyl and propyl esters, and also *methyl diphenyl- α -isobutyryl-telluretine bromide* [α -bromodiphenyltelluriisobutyrate],



are white, amorphous substances with indefinite melting points.

J. C. W.

1-Benzoyl-2-phenyl- Δ^2 -cyclopentene. ÉDOUARD BAUER (*Compt. rend.*, 1913, 156, 1470—1472).—The conversion of α,α -dibenzoylbutane into the two cyclic compounds 1-benzoyl-2-phenyl- Δ^1 - and Δ^2 -cyclopentenes by the action of sodium ethoxide (compare A., 1912, i, 777) is equally well brought about by sodamide. 1-Benzoyl-2-phenyl- Δ^2 -cyclopentene, thus constituted, should behave as a dialkylacetophenone (compare Haller and Bauer, A., 1909, i, 108), and the author has now proved this to be the case. It reacts with sodamide in anhydrous benzene, giving a sodium derivative which, on the addition of methyl iodide, is converted into the corresponding 1-benzoyl-2-phenyl-1-methyl- Δ^2 -cyclopentene (formula II), b. p. 223—224°/23 mm., a viscid oil instantly decolorising potassium permanganate solution in the cold. This



methyl derivative reacts further with sodamide (compare Haller and Bauer, *loc. cit.*) and is decomposed, giving a mixture of 2-phenyl-1-methyl- Δ^2 -cyclopentene (formula III), b. p. 116—117°/20 mm., and benzamide on the one hand, and benzene and 2-phenyl-1-methyl- Δ^2 -cyclopentene-1-carboxylamide (formula IV), m. p. 165°, on the other.

W. G.

1-Benzoyl-2-phenyl- Δ^1 -cyclopentene. ÉDOUARD BAUER (*Compt. rend.*, 1913, 156, 1684—1686. Compare A., 1912, i, 777; preceding abstract).—Sodamide acts on 1-benzoyl-2-phenyl- Δ^1 -cyclopentene in the same manner as on benzophenone (compare A., 1908, i, 987), giving 2-phenyl- Δ^1 -cyclopentene-1-carboxylamide and benzene and 1-phenyl- Δ^1 -cyclopentene and benzamide.

On boiling 1-benzoyl-2-phenyl- Δ^1 -cyclopentene with sodamide in benzene a brick-red precipitate is obtained, which is decolorised on treatment with water. This product is separable by crystallisation from ether into benzamide and 2-phenyl- Δ^1 -cyclopentene-1-carboxylamide, needles, m. p. 135—136°, which rapidly reduces alkaline permanganate

and decolorises bromine in chloroform. On hydrolysis with alcoholic potassium hydroxide it yields a mixture of two isomeric acids,



separable by crystallisation from ether into 2-phenyl- Δ^1 -cyclopentene-carboxylic acid, m. p. 157°, and an acid, m. p. 124–125°, differing from the other only in the position of the ethenoid linking in the nucleus, and which gives the corresponding amide, m. p. 178–179°.

From the original benzene solution, after distilling off the solvent, there is obtained 1-phenyl- Δ^1 -cyclopentene, m. p. 23°, b. p. 120–121°/20 mm., D_4^{20} 0.98617, n_D^{20} 1.56723, n_D^{25} 1.5734, n_D^{28} 1.59017, which yields a picrate, m. p. 64.5°. On reduction by sodium in absolute alcohol it gives phenylcyclopentane.

W. G.

Preparation of Nitriles from Thiocarbamides [and from Thiocarbimides]. FARBENFABRIKEN VÖRM. FRIEDR. BAYER & Co. (D.R.-P. 259363, 259364).—It has been shown by Weith (A., 1875, 901, 908, 1241) that nitriles (in very small yield) can be obtained by the action of copper powder on thiocarbamides, and this reaction has now been carried out with cheaper material, such as iron, in the presence of machine oil or paraffin oils or anthracene.

o-Toluenitrile is obtained in 64% yield when a mixture of iron (20 parts) and paraffin (100 parts) is slowly treated at 280° with 10 parts of *o*-ditolylthiocarbamide. The preparation of the following compounds is also described: *m*-toluenitrile in 62% yield, *p*-toluenitrile in 75% yield, β -naphthonitrile in 75% yield, *m*-xylonitrile in 65% yield, *p*-methoxybenzonitrile in 67% yield, *p*-chlorobenzonitrile in 51% yield from *p*-dichlorophenylthiocarbamide, *p*-cyanoquinoline in 21% yield from *p*-diquinolythiocarbamide, octonitrile in 61% yield from diheptylthiocarbamide, and phenylacetone in 20% yield from dibenzylthiocarbamide.

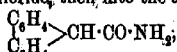
The second patent describes the preparation of many of the preceding compounds by substituting the corresponding thiocarbimides for the thiocarbamides, the average yield of product being about the same.

F. M. G. M.

Polymerisation. ABRAHAM KRONSTEIN (*Ber.*, 1913, 46, 1812–1814).—A claim for priority in the study of polymerisation from the chemical, physical, technical, and also physiological points of view (compare Liebermann and Kardos, this vol., i, 476). J. C. W.

Preparation of Diphenyleneacetic Acid (9-Fluorene-carboxylic Acid) from Benzilic Acid and Aluminium Chloride. DANIEL VORLÄNDER and ALFRED PRITZSCHE (*Ber.*, 1913, 46, 1793–1796).—The fact that Vorländer and Huth assumed the formation of the unknown nitrile of benzilic acid as an intermediate stage in the condensation of benzoyl cyanide to 9-cyanofluorene (A., 1911, i, 867) has led to the study of benzilic acid itself, with the result that a good method for the preparation of 9-fluorene-carboxylic acid has been discovered. Triphenylacetic acid could not be detected in the product, and therefore diphenylchloroacetic acid cannot represent an intermediate stage. Carbon disulphide, or preferably benzene, may be used as a solvent, but they do not enter into the reaction. The fluorene-

carboxylic acid was characterised by conversion into the unstable chloride with thionyl chloride, then into the *amide*,



microscopic needles, m. p. 250°, and finally into the nitrile (Wislicenus and Russ, A., 1910, i, 840).

Phenylglyoxylic acid also condenses with benzene in presence of aluminium chloride, forming benzilic acid, and subsequently the above 9-fluorencarboxylic acid. Ethyl phenylglyoxylate gives the same result, whereas the action of magnesium phenyl bromide leads to the formation of ethyl benzilate and, with an excess, benzopinacolone. In toluene solution, phenylglyoxylic acid condenses to *p-methylfluorencarboxylic acid*, $\text{C}_{15}\text{H}_{12}\text{O}_2$, which has m. p. 210°, and yields *p-methylfluorene* in leaflets, m. p. 88°, on distillation with soda-lime.

The alkaline solution of the condensation product of diphenylenglycollic acid and benzene has a violet fluorescence and contains a little 9-phenylfluorencarboxylic acid, $\text{C}_{20}\text{H}_{14}\text{O}_2$, which crystallises in white needles, m. p. 183°, and is easily transformed into 9-phenylfluorene (Kriegel, A., 1905, i, 187).

J. C. W.

Pimaric Acid. LEO A. TSCHUGAEV and P. TCHERU (*Ber.*, 1913, 46, 1769—1774. Compare Vesterberg, A., 1886, 365, 1038; 1888, 249; 1906, i, 92; 1907, i, 213).—The authors confirm Vesterberg's conclusion that galipot must contain at least three acids. *d*-Pimaric acid has m. p. 211—212°, $[\alpha]_D^{20} + 55.40^\circ$, $[\alpha]_D^{25} + 72.52^\circ$, $[\alpha]_D^{30} + 97.20^\circ$, $[\alpha]_D^{35} + 123.0^\circ$, $[\alpha]_D^{40}/[\alpha]_D^{20}$ 2.20°. 2.129 Grams of acid are soluble in 100 grams of absolute methyl alcohol at 25°. The acid is monobasic. The sodium salt has $[\alpha]_D^{20} + 30.12^\circ$, $[\alpha]_D^{25} + 38.86^\circ$, $[\alpha]_D^{30} + 52.42^\circ$, $[\alpha]_D^{35} + 67.37^\circ$, $[\alpha]_D^{40}/[\alpha]_D^{20}$ 2.23° in methyl-alcoholic solution ($c = 2.174$). Methyl pimarate, m. p. 69°, obtained by the action of methylsulphate on an aqueous alcoholic solution of sodium pimarate in the presence of an excess of sodium hydroxide or carbonate, has $[\alpha]_D^{20} + 46.30^\circ$, $[\alpha]_D^{25} + 60.45^\circ$, $[\alpha]_D^{30} + 81.36^\circ$, $[\alpha]_D^{35} + 102.7^\circ$, $[\alpha]_D^{40}/[\alpha]_D^{20}$ 2.22.

In the presence of spongy platinum, hydrogen converts *d*-pimaric acid into *dihydropimaric acid*, m. p. 240—241°; 100 grams of absolute methyl alcohol dissolve 0.478 gram acid. In ethyl alcoholic solution ($c = 0.566$) at 20° the latter has $[\alpha]_D^{20} + 14.57^\circ$, $[\alpha]_D^{25} + 19.43^\circ$, $[\alpha]_D^{30} + 26.05^\circ$, $[\alpha]_D^{35} + 37.53^\circ$, $[\alpha]_D^{40}/[\alpha]_D^{20}$ 2.57. It is monobasic, and forms salts closely resembling those of pimaric acid. The sodium salt has in methyl alcoholic solution ($c = 3.568$) at 20°, $[\alpha]_D^{20} + 4.41^\circ$, $[\alpha]_D^{25} + 5.46^\circ$, $[\alpha]_D^{30} + 7.84^\circ$, $[\alpha]_D^{35} + 11.14^\circ$, $[\alpha]_D^{40}/[\alpha]_D^{20}$ 2.56. The ammonium salt crystallises in long, thin needles.

The authors consider that pimaric acid is probably a tetracyclic compound with one double bond.

H. W.

Preparation of Phenolcarboxylic Acids. JOSEPH ZELTNER and MAX LANDAU (D.R.P. 258887. Compare A., 1876, ii, 632; 1877, i, 77; ii, 415).—The action of chloroform or carbon tetrachloride on phenols has been studied (*loc. cit.*), and the reaction is, now found to proceed smoothly under atmospheric pressure in the presence of copper powder, or a salt of copper.

When phenol (9.4 parts), a 40% solution containing potassium hydroxide (39.2 parts), carbon tetrachloride (16 parts), and 0.3 part of copper, are boiled together during eight hours under reflux, it gives rise to a mixture of salicylic acid (25%) and *p*-hydroxybenzoic acid (30%).

The preparation of the following compounds is also described: 4-hydroxy-*m*-toluic acid, m. p. 146–147°, in 60% yield from *p*-cresol; an 80–85% yield of a mixture of 6- and 4-hydroxy-*m*-toluic acids from *o*-cresol. A 45% yield of 3-nitrosalicylic acid (compare Hasse, *loc. cit.*) from *o*-nitrophenol; and of 5-chlorosalicylic acid (in 75% yield) from *p*-chlorophenol. Guaiacol furnished vanillic acid, m. p. 207°, and quinol gave rise to gentisic acid. Salicylic acid gave a 70–75% yield of a mixture of phenol-2:4- and 2:6-dicarboxylic acids separable by means of their barium salts, whilst *m*-cresotic acid furnished α -coccinic acid (A., 1897, i, 539), and *o*-cresotic acid yielded 1-hydroxy-2-methylbenzene-4:6-dicarboxylic acid (α -hydroxyuvitic acid), m. p. 294–295°.

F. M. G. M.

Preparation of Acetylcarbiny *o*-Thymotate. ADOLF DIEFFENBACH and RICHARD ZAHN (D.R.-P. 258936).—The methyl and ethyl esters of *o*-thymotic acid are known (A., 1910, i, 38), and acetylcarbiny *o*-thymotate, m. p. 75° (annexed formula), has now been prepared by the action of monochloroacetone on sodium *o*-thymotate.

F. M. G. M.

α -Hydroxy- γ -phenylcrotonic Acid; its Preparation; New Isomerisation. J. BOUGAULT (*Compt. rend.*, 1913, 156, 1468–1470. Compare A., 1912, i, 770; this vol., i, 269).— α -Hydroxy- γ -phenylcrotonic acid is most readily prepared from its amide by choice of suitable hydrolysing agents, which will not bring about its isomerisation into benzylpyruvic or benzoylpropionic acids. Aqueous solutions of alkali carbonates or hydrogen carbonates boiled for thirty to forty minutes with the amide convert 30–40% into the acid required, with only a small admixture of its isomerides. As acid hydrolysing agents, the best are aqueous solutions of oxalic or phosphoric acids, oxalic acid (7½%) giving a yield of 80% of the acid required.

The author has isolated a new isomeride, m. p. 91°, which appears to be the *enolic* form of benzoylpropionic acid, and to have the constitution $C_6H_5 \cdot C(OH) : CH \cdot CH_2 \cdot CO_2H$. It is readily converted by alkalis and strong acids into the ketonic form.

W. G.

Preparation of Halogen Alkyl Esters of *o*-Acetoxybenzoic Acid. RICHARD WOLFFENSTEIN (D.R.-P. 258888. Compare A., 1912, i, 556, 768).—The crystalline ester, $OAc \cdot C_6H_4 \cdot CO \cdot O \cdot CHMe \cdot CCl_3$, m. p. 52°, is obtained when *o*-acetoxybenzoyl chloride is heated with trichloroisopropyl alcohol in the presence of dimethylaniline, whilst the tribromo-*tert*-butyl *o*-acetoxybenzoate, m. p. 90°, is prepared by the action of *o*-acetoxybenzoyl chloride on acetonebromoform [tribromo-*tert*-butyl alcohol], $OH \cdot CMe_2 \cdot CBr_3$, and the compound formed when the latter constituent is replaced by dichloroisobutyl alcohol is also mentioned.

F. M. G. M.

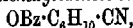
Benzoylcyanohydrins of Ketones, and Amides, and Hydroxy-acids Derived from Them. JULES ALOY and CHARLES RABAUT (*Compt. rend.*, 1913, 156, 1547—1549. Compare A., 1912, i, 462).—Benzoylcyanohydrins can be readily obtained from ketones by the gradual addition of benzoyl chloride (1/10th mol.) to a solution of potassium cyanide (1/10th mol.) in 100 c.c. of water containing the ketone (1/10th mol.). The mixture is shaken for three hours and then extracted with ether, from which the cyanohydrin crystallises. They are, in general, quite crystalline and stable, and are hydrolysed by sulphuric acid, giving the corresponding benzoylamide, which is further hydrolysed by sodium hydroxide to benzoic acid and the hydroxy-acid.

Thus acetone gives *propylidenbenzoylcyanohydrin*, $\text{OBz}\cdot\text{CMe}_2\cdot\text{CN}$, m. p. 36—37°, yielding the *amide*, $\text{OBz}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NH}_2$, m. p. 142—143°, which is hydrolysed to *α-hydroxy-α-methylpropionic acid*, m. p. 79°.

Methyl propyl ketone yields *β-amyldenbenzoylcyanohydrin*, a syrupy liquid, hydrolysing to the *benzoylamide*, m. p. 126°, which on further hydrolysis yields *α-hydroxy-α-methylvaleric acid*, $\text{OH}\cdot\text{CPrMe}\cdot\text{CO}_2\text{H}$, m. p. 46—47°.

Diethyl ketone gives a small yield of *γ-amyldenbenzoylcyanohydrin*, a liquid, which furnishes an *amide*, $\text{OBz}\cdot\text{CEt}_2\cdot\text{CO}\cdot\text{NH}_2$, m. p. 149—150°.

cyclohexanone gives *cyclohexyldenbenzoylcyanohydrin*,



m. p. 71°, yielding an *amide*, m. p. 118°, which is hydrolysed to *cyclohexanol-1-carboxylic acid*.

3-Methylcyclohexanone gives a *benzoylcyanohydrin*, m. p. 125—126°, yielding the *amide*, m. p. 135—136°, which on hydrolysis gives 3-methylcyclohexanol-1-carboxylic acid.

4-Methylcyclohexanone is converted into the *benzoylcyanohydrin*, m. p. 86°, this giving an *amide*, m. p. 122°, which finally yields 4-methylcyclohexanol-1-carboxylic acid, m. p. 80—81°. W. G.

The Action of Nitric Acid on the Dihydroxybenzoic Acids. FRANZ VON HEMMELMAYR (*Monatsh.*, 1913, 34, 811—820).—Of the dihydroxybenzoic acids it is not the compound in which the carboxyl group is most firmly attached which can be nitrated most satisfactorily, but the important condition apparently is resistance to oxidation by the nitric acid; for example, β-resorcylic acid can be nitrated successfully, whilst gentisic acid, the nitro-derivative of which is much more stable, is for the greater part oxidised to oxalic acid. The author has therefore compared the behaviour of these acids towards nitric acid (D 1·4), and finds that the acids derived from catechol and quinol are oxidised almost entirely to oxalic acid. It is an interesting fact that those acids in which the meta-positions are unoccupied and in which at least one of these vacant positions is in a para-position to a hydroxy-group, more readily undergo nitration (compare von Hemmelmayr, this vol., i, 468).

3,4-Dihydroxybenzoic (protocatechuic) acid with the nitric acid alone or in acetic acid solution gave much oxalic acid, together with orange-red needles of a substance, $\text{C}_6\text{O}_{10}\text{N}_4$, possibly tetranitro-o-benzoquinone.

2:3-Dihydroxybenzoic acid gave a vigorous reaction with production of oxalic acid.

3:5-Dihydroxybenzoic (α -resorcylic) acid reacted vigorously, giving mainly oxalic acid together with a small quantity of an impure yellow, crystalline substance. By allowing the nitration to proceed in ethereal solution, the oxidising effect of nitric acid is diminished, and a nitro-3:5-dihydroxybenzoic acid, deep red needles, m. p. 210° (decomp.), could be isolated in small quantity.*

2:6-Dihydroxybenzoic (γ -resorcylic) acid gave a vigorous reaction from the product of which a trinitrohydroxybenzoic acid, brownish-red, microscopic needles, decomp. at 240°, could be isolated.

2:5-Dihydroxybenzoic (gentisic) acid, when nitrated in cold ethereal solution, gave an approximately 30% yield of nitrogentisic acid (compare Klemenc, this vol., i, 49), which crystallises with 2H₂O.

D. F. T.

Preparation of Anthraquinone- α -carboxylic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 259365. Compare A., 1911, i, 279; 1912, i, 979; this vol., i, 49).—1-Chloroanthraquinone-4-carboxylic acid, m. p. 229—230°, is prepared by heating together phthalic anhydride and *p*-chlorotoluene in nitrobenzene solution, and introducing chlorine at a temperature of 160—170°.

When phthalic anhydride and *m*-xylene are condensed in the presence of chlorine, they furnish 3-methylanthraquinone-1-carboxylic acid, m. p. 246—247°, and apparently identical with that previously prepared by Wachendorff and Zincke (A., 1878, 232), whilst oxidation of the sodium salt with potassium permanganate furnishes anthraquinone-1:3-dicarboxylic acid, m. p. above 300°.

F. M. G. M.

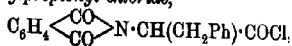
Preparation of Phenylmethylphthalide. ALFONS OSTERSETZER (*Monatsh.*, 1913, 34, 795—796).—From analogy to the behaviour of the *o*-aldehydic acids which yield alkyl substituted phthalides (Mermod and Simonis, 1908, i, 342; Simonis, Marben and Mermod, 1906, i, 32), it might be expected that *o*-ketonic acids when treated with a Grignard reagent should yield dialkyl substituted phthalides.

The reaction product of *o*-benzoylbenzoic acid and magnesium phenyl bromide is an oil, but magnesium methyl iodide gave phenylmethylphthalide, C₆H₄ < $\begin{smallmatrix} \text{CMePh} \\ \text{CO} \end{smallmatrix} \rangle$ O, leaflets, m. p. 76°; the intermediate hydroxy-acid could not be isolated.

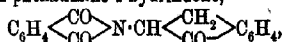
D. F. T.

The Action of Phthalylacetyl Chlorides on Benzene and Aluminium Chloride. ERNST PFAEHLER (*Ber.*, 1913, 46, 1700—1702).—Although phthalylphenylglycyl chloride (Pfaehler, this vol., i, 751) behaves similarly to phthalylglycyl chloride and the aliphatic homologues of this substance towards benzene and aluminium chloride, some of its higher homologues, such as phthaliminophenylpropionyl chloride, act in a different manner.

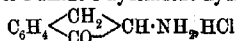
Phthaliminophenylpropionyl chloride,



m. p. 131–132°, was obtained from the corresponding acid, m. p. 176–177°, which is produced when phthalaminobenzylmalonic acid, m. p. 160–170° (compare Sörensen, A., 1903, i, 834), is heated. When warmed with an equimolecular quantity of aluminium chloride in benzene solution, 2-phthalimino-1-hydrindone,



m. p. 191°, is obtained by intramolecular elimination of hydrogen chloride; it was not found possible to produce this substance by direct dehydration of the free acid. By heating the phthaliminohydrindone in acetic acid solution with fuming nitric acid at first in the open and afterwards in a sealed tube at 135°, the phthalyl nucleus is oxidised with the production of 2-amino-1-hydrindone hydrochloride,



(compare Gabriel and Stelzner, A., 1897, i, 61).

D. F. T.

Hydrogenation of Santonic Acid. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 507–510).—When sodium santonate is treated with hydrogen in presence of platinum-black until no more gas is absorbed, a tetrahydrosantononic acid, $\text{C}_{18}\text{H}_{24}\text{O}_4$, is formed; it crystallises in prisms or in leaflets, m. p. 190° (decomp.). The same tetrahydro-derivative was obtained in an experiment in which only one-fourth of the requisite amount of hydrogen was employed, and a corresponding quantity of santonate remained unaltered. In this experiment was also isolated a small quantity of a substance, which formed acicular prisms, m. p. about 99°, and gave a green fluorescence with alcoholic potassium hydroxide. This compound of m. p. 99° gives an oxime, which crystallises in lustrous needles, m. p. about 235°. Tetrahydrosantononic acid dissolves in carbonates in the cold, gives no coloration with alcoholic potassium hydroxide, and has no bitter taste. When treated with acids it loses water. It dissolves readily in concentrated hydrochloric acid; the solution becomes greenish-brown, and if left exposed to the air deposits a substance, which after recrystallisation forms large, colourless, prismatic crystals, m. p. 88°. This compound does not dissolve in carbonates in the cold, but when its alkaline solution (obtained in the warm) is acidified, an acid separates in laminar crystals, which at first have m. p. about 130°, but after exposure to the air acquire the m. p. of tetrahydrosantononic acid. The substance of m. p. 88° crystallises from light petroleum in laminae or in prisms of m. p. 102°, and these are converted into tetrahydrosantononic acid by boiling with potassium hydroxide. Conversely, if tetrahydrosantononic acid is boiled with *N*-sulphuric acid the substance of m. p. 102° is obtained. Tetrahydrosantononic acid yields an oxime, which crystallises in colourless prisms, m. p. 222° (decomp.), and on boiling with dilute sulphuric acid yields the above-mentioned compound of m. p. 102°. When an acetic acid solution of the oxime is treated with nitrous acid, a crystalline compound of m. p. 130° is formed; it yields a blue coloration with a sulphuric acid solution of diphenylamine. On treatment with concentrated sulphuric acid the oxime is converted into a substance which crystallises in rectangular tablets,

m. p. 235° (not sharply); this compound does not dissolve in carbonates in the cold, and it reduces Fehling solution after hydrolysis with acid. The two oximes which have been mentioned can be obtained directly from the raw product of the hydrogenation, but together with them there is then observed a third *oxime*, which forms small, colourless needles, m. p. 240° (decomp.). From alkali solutions of this substance sulphuric acid precipitates a *compound*, crystallising in regular, hexagonal laminae, m. p. 160—162°.

R. V. S.

Hydrogenation of Santonin. YASUHIKO ASAHINA (*Ber.*, 1913, 46, 1775—1777).—*Tetrahydrosantonin*, $C_{15}H_{22}O_3$, is formed by the action of hydrogen on a solution of santonin in glacial acetic acid in the presence of platinum-black. It consists of thin, white leaflets,

m. p. 155—156°, $[\alpha]_D^{25} + 60.56^\circ$, in chloroform solution. It yields a clear solution after protracted boiling with saturated aqueous barium hydroxide, from which the original substance is reprecipitated on acidification, and thus contains the lactonic group intact. In glacial acetic acid solution, it is stable towards permanganate. It yields an *oxime*, $C_{15}H_{25}NO$, m. p. 225°, $[\alpha]_D^{25} - 17.78^\circ$, in chloroform solution.

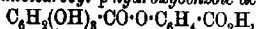
The author is led to the conclusion that the annexed formula for santonin most readily harmonises with the above data.

H. W.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. IX. Derivatives of Pyrogallolcarboxylic Acid. EMIL FISCHER and MAX RAPAPORT (*Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 493—506).—When an excess of methyl chloroformate is allowed to act on pyrogallolcarboxylic acid the trimethylcarbonato-compound is obtained. Phosphorus pentachloride converts it into the corresponding chloride, which crystallises from ether and has been used for the following synthetic operations.

Benzene and aluminium chloride convert it into a product yielding 2:3:4-trihydroxybenzophenone on hydrolysis, which is identical with the dye alizarin-yellow-A; the structure of this is thus established.

By interaction of the chloride in alkaline solution with *p*-hydroxybenzoic acid and subsequent elimination of the methylcarbonato-groups the dipeptide, *pyrogallolcarboyl-p-hydroxybenzoic acid*,



isomeric with galloyl-*p*-hydroxybenzoic acid is obtained.

The new term, *carboyl*, denoting the carboxylic acid radicle is derived in a similar way to benzoyl from benzoic acid—the radicle of pyrogallolcarboxylic acid is thus pyrogallolcarboyl.

When dextrose is shaken with the chloride and quinoline in chloroform solution, five trimethylcarbonatopyrogallolcarboyl residues are introduced into the sugar. On cautious hydrolysis a tannin is obtained isomeric with pentagalloyldextrose.

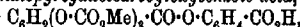
Trimethylcarbonatopyrogallolcarboxylic acid, $C_6H_2(O \cdot CO_2Me)_5 \cdot CO_2H$,

crystallises in tiny, colourless platelets, m. p. 122—124° (corr.). The pure acid gives hardly any coloration with ferric chloride.

The corresponding *chloride* crystallises in colourless, lancet-shaped needles, m. p. 67—68° (corr.).

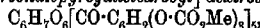
The *methyl* ester, $C_6H_4(O\cdot CO_2Me)_2\cdot CO_2Me$, crystallises in microscopic, stout double pyramids, m. p. 82—84°, the homologous *ethyl* ester crystallises in tiny, oblique plates, m. p. 91—94° (corr.).

Trimethylcarbonatopyrogallolcarboylbenzoic acid,



crystallises in slender, microscopic platelets, m. p. 198—199° (corr.). Ammonia converts it into *pyrogallolcarboyl-p-hydroxybenzoic acid*, $C_6H_2(OH)_3\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$. The diester crystallises in very small, lustrous crystals aggregated in bunches, m. p. 235—238° (corr., decomp.). With ferric chloride a blue or bluish-violet coloration is produced.

Penta-[trimethylcarbonatopyrogallolcarboyl]-dextrose,



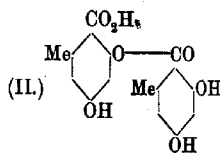
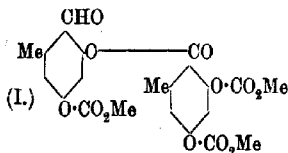
forms a colourless, amorphous powder which sinters at 100°, m. p. about 130°, $[\alpha]_D^{25} + 27^\circ$.

Pentapyrogallolcarboylglucose forms also a colourless, amorphous powder, which sinters about 160°, m. p. 200° (decomp.), $[\alpha]_D^{25} + 69.1^\circ$. It differs from tannic acid and pentagalloylglucose in being sparingly soluble in water.

E. F. A.

Synthesis of *o*-Diorsellinic Acid. EMIL FISCHER and HERMANN O. L. FISCHER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 507—512).—Two diesters are derived from orsellinic acid according as coupling takes place in the ortho- or para-positions. The product previously obtained (this vol., i, 477), identical with the natural lecanoric acid, was considered to be the *p*-diorsellinic acid, and this is now confirmed by the synthesis of the ortho-isomeride.

Methylcarbonato-orsellaldehyde (Hoesch, this vol., i, 474) is readily coupled with dimethylcarbonato-orsellinyl chloride in alkaline solution, yielding the following compound (I). The corresponding acid is



obtained on oxidation with permanganate, and it is converted into the *o*-diorsellinic acid on elimination of the methyl carbonato-groups by means of dilute ammonia. The *o*-diorsellinic acid (II) differs from lecanoric acid in solubility, melting point, and in its behaviour towards ferric chloride. It differs also from the gyrophoric acid described by Hesse (A., 1901, i, 151).

Trimethylcarbonato-orsellinoylorcylaldehyde crystallises in slender, pliable needles, m. p. 112—113° (corr.).

Trimethylcarbonato-o-diorsellinic acid separates in tiny, six-sided

platelets which sinter at 150° , m. p. 158° (corr., decomp.). With ferric chloride only a yellow coloration is obtained.

o-Dioresellinic acid (formula II) forms colourless, tiny needles much intergrown, but appears somewhat yellow in bulk. It has m. p. $120-125^{\circ}$, becomes solid, and melts again at $180-185^{\circ}$. E. F. A.

Angeli-Rimini Reaction of the Aldehydes. LUIGI BALBIANO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 575-579).—Polemical. A reply to Angeli (A., 1912, i, 626). R. V. S.

Quantitative Investigation of the Photochemical Transformation of *o*-Nitrobenzaldehyde into *o*-Nitrosobenzoic Acid. ANTON KAILAN (*Ber.*, 1913, 46, 1628-1634).—Polemical. The author maintains the sufficiency of his methods and the accuracy of the results obtained by him (this vol., i, 51) against the criticism of Weigert and Kummerer (this vol., ii, 370). R. V. S.

Some Derivatives of Methylcyclopentan-3-one. MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1913, 156, 1779-1781. Compare this vol., i, 278).—By the action of dry chlorine on methylcyclopentan-3-one in diffused light at a temperature below 25° , 2-chloromethylcyclopentan-3-one, C_5H_9OCl , is obtained as a colourless oil, b. p. $80-82^{\circ}/8$ mm., D_4^{20} 1.128, n_D^{20} 1.465. On boiling this chloro-derivative with water it yields a mixture of methylcyclopentan-2-ol-3-one, b. p. $83-85^{\circ}/12$ mm., and 2-methyl- Δ^1 -cyclopenten-5-one, b. p. $50^{\circ}/12$ mm. The former of these compounds is a pale yellow, syrupy liquid, giving a violet coloration with ferric chloride, and yielding an unstable phenylhydrazones. On oxidation the ketone-alcohol is converted into α -methylglutaric acid. 2-Methyl- Δ^1 -cyclopenten-5-one is a colourless liquid, having b. p. $157-158^{\circ}$, D_4^{20} 0.9712, n_D^{20} 1.4714. It is very soluble in water, and gives a semicarbazone, m. p. 230° , and an oxime, m. p. 127° . W. G.

Reduction of Ketones and Aldehydes to the Corresponding Hydrocarbons by means of Amalgamated Zinc and Hydrochloric Acid. ERIK CLEMMENSEN (*Ber.*, 1913, 46, 1837-1843).—The application of amalgamated zinc has led to very good results in the reduction of fatty-aromatic ketones, and of aliphatic ketones and aldehydes to the corresponding hydrocarbons. In practice, an excess of granulated zinc is left for an hour with 5% mercuric chloride, drained, and then heated with the substance and concentrated hydrochloric acid under reflux, care being taken that the evolution of hydrogen is brisk enough to keep the two liquids well mixed.

By this means acetophenone gives ethylbenzene, or by using only the theoretical amount of acid, styrene. Propiophenone or phenylacetone give 90% yields of *n*-propylbenzene; butyrophenone or benzylacetone give 88-100% yields of *n*-butylbenzene, and methyl α -naphthyl ketone is reduced to α -ethylnaphthalene. Aromatic aldehydes are too susceptible to the action of mineral acids, but, notwithstanding, a 46%

yield of toluene was obtained from benzaldehyde. Heptaldehyde, however, gives a good yield of *n*-heptane. The following reductions of aliphatic ketones give almost theoretical yields; methyl *n*-nonyl ketone to *n*-undecane, methyl *n*-heptadecyl ketone to *n*-nonadecane, di-*n*-heptadecyl ketone (stearone) to *n*-pentatriacontane. The method is being extended to other classes of compounds. J. C. W.

Dynamic Isomerism. HENRY E. ARMSTRONG, THOMAS M. LOWRY, SIDNEY YOUNG, CECIL H. DESCH, JAMES J. DOBBIE, MARTIN O. FORSTER, and ARTHUR LAPWORTH (*Rep. Brit. Assoc.*, 1912, 115—116).—See Lowry and Glover, T., 1913, 103, 913. C. H. D.

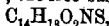
Synthesis of Violanthrone. CHRISTIAN SEER and ROLAND SCHOLL (*Annalen*, 1913, 398, 82—96).—The constitution of violanthrone has been now proved, since the orientation of the benzoyl groups in the dibenzoyl-*aa*-dinaphthyl used in its synthesis (this vol., i, 59) has now been definitely settled.

aa-Naphthidine in 3% hydrochloric acid at 0° is treated with sodium nitrite, and the tetrazotised solution is filtered into aqueous potassium cyanide and copper sulphate at 60°, whereby 4:4'-*dicyano-a-a*-di-naphthyl, m. p. 280—281°, pale yellow needles, is obtained. The latter is hydrolysed by alcoholic sodium hydroxide at 160—190°, and the resulting *aa*-dinaphthyl-4:4'-dicarboxylic acid, m. p. 349—350°, colourless crystals, is converted by phosphoric and phosphoryl chlorides into the acid dichloride, pale brown crystals, from which 4:4'-dibenzoyl-*aa*-dinaphthyl is obtained by means of aluminium chloride and benzene in nitrobenzene at 70—75°. 4:4'-Dibenzoyl-*aa*-dinaphthyl has now been prepared in orange-yellow needles, m. p. 146—147°; it is converted into violanthrone by aluminium chloride at 95—100° (*loc. cit.*).

By treatment with hydriodic acid, b. p. 127°, and red phosphorus at 190° for ten hours, violanthrone is converted into a substance which is apparently its parent hydrocarbon, *violanthrene*, $C_{24}H_{20}$; it is a dark powder which is not attacked by alkaline sodium hyposulphite, and forms in concentrated sulphuric acid a blue solution with a brown fluorescence.

5-Iodo-1-naphthoic acid, m. p. 253—254°, colourless needles, prepared in the usual manner from 5-amino-1-naphthoic acid, forms a methyl ester, $C_{12}H_9O_2I$, m. p. 81—82°. By heating the latter with copper powder at 220—240° in a current of carbon dioxide, methyl *aa*-di-naphthyl-5:5'-dicarboxylate, $C_{24}H_{18}O_4$, m. p. 173—174°, faintly yellow needles, is obtained. The acid, $C_{22}H_{16}O_4$, m. p. 359—360°, microscopic needles, is converted into the crude chloride, m. p. about 150°, by phosphorus pentachloride, and the chloride is heated with aluminium chloride, benzene, and nitrobenzene at 70—80°, whereby 5:5'-dibenzoyl-*aa*-dinaphthyl, $C_{34}H_{26}O_2$, m. p. 248—250°, glistening leaflets, is obtained. By heating the latter with aluminium chloride at 145°, neither *Bz*-1:1'-dibenzanthronyl nor violanthrone is produced, but benzanthrone; whether this is present as such in the crude 5:5'-dibenzoyl-*aa*-dinaphthyl or is produced during the reaction was not determined. C. S.

Conversion of 3-Dimethylaminophenyl Methyl Sulphide into 3-Methylthiol-*p*-benzoquinone. THEODOR ZINCKE and JOHANNES MÜLLER (*Ber.*, 1913, 46, 1777—1781. Compare this vol., i, 355).—3-Methylthiol-4-nitrosodimethylaniline hydrochloride separates in red needles when a solution of sodium nitrite is added to a well-cooled solution of 3-dimethylaminophenyl methyl sulphide in hydrochloric acid. The free base is best obtained by addition of sodium acetate, and forms green needles melting at 143° to a deep blue liquid. When boiled with *N*-sodium hydroxide, it yields dimethylamine and 4-nitroso-3-methylthiolphenol, yellow needles, m. p. 186°, which is converted by acetic anhydride and sodium acetate into the corresponding acetyl derivatives, yellow needles, m. p. 165°. 4-Amino-3-methylthiolphenol is obtained by reduction of a boiling ammoniacal solution of 4-nitroso-3-methylthiolphenol by hydrogen sulphide, and, after purification by sublimation in a vacuum, forms nearly colourless needles, m. p. 154°, which readily oxidise on exposure to air. The alkali salts and the hydrochloride are readily soluble; the sulphate is more sparingly soluble. The diacetyl derivative forms small, white crystals, m. p. 100°, which contain $\frac{1}{2}$ mol. acetic acid. When warmed with salicylaldehyde in alcoholic solution, the free base yields a substance,



yellowish-brown needles, m. p. 134°.

3-Methylthiol-*p*-benzoquinone (annexed formula) is obtained by addition of dichromate solution to a solution of 4-amino-3-methylthiolphenol in dilute sulphuric acid and subsequent oxidation of the bluish-black product so obtained with nitric acid in acetic acid solution. An excess of nitric acid causes the elimination of the methylthiol group.

It is therefore preferable to reduce the above quinhydrone to the quinol and oxidise the latter with dilute sulphuric acid and dichromate solution. 3-Methylthiol-*p*-benzoquinone forms red needles, m. p. 148°. Concentrated nitric acid (D 1.4) dissolves it without change; sulphurous acid reduces it to the corresponding quinol. When dissolved in chloroform and treated with chlorine, it gives tetrachloro-*p*-benzoquinone, whilst with aniline in hot glacial acetic acid solution it yields 2:5-dianilino-*p*-benzoquinone and methyl mercaptan.

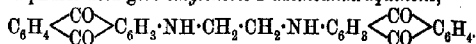
3-Methylthiolquinol forms white needles, m. p. 83°, which are readily oxidised on exposure to air. With acetic anhydride and sodium acetate it yields a diacetyl compound, m. p. 101°.

H. W.

2-Aminoanthraquinone. FRITZ ULLMANN and ROBERT MEDENWALD (*Ber.*, 1913, 46, 1798—1809).—Two iminoanthraquinone nuclei have been linked together by an ethylene group, the sulphonic acid derived from aminoanthraquinone has been shown to be the 3-sulphonic acid, the preparation of the 1-nitro- and 3-nitro-2-aminoanthraquinones is described, and the condensation of 1:3-dibromo-2-aminoanthraquinone with bases has been studied.

Toluene-*p*-sulpho-2-anthraquinonylamide, $\text{C}_{14}\text{H}_7\text{O}_2\text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4$, from 2-aminoanthraquinone and *p*-toluenesulphonylchloride in pyridine,

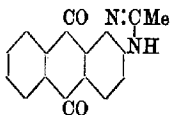
forms yellow needles, m. p. 304° (corr.), which give a red solution in hot alkalis or cold concentrated sulphuric acid. Excess of the sulphonyl chloride gives rise to the *disulphonamide*, $C_{28}H_{21}O_6NS_2$, in yellowish-brown crystals, m. p. 256° (corr.), whereas methyl sulphate yields *toluene-p-sulpho-2-anthraquinonylmethylamide* in yellow crystals, m. p. 195° (corr.), from which 2-methylaminoanthraquinone, $C_{14}H_9O_2 \cdot NHMe$, may be obtained in long, ruby-red needles, m. p. $226-227^{\circ}$ (corr.), by warming with concentrated sulphuric acid. When condensed with ethylene dibromide in a sealed tube, the original sulphonamide yields *ethylenebistoluene-p-sulpho-2-anthraquinonylamide*, $C_{14}H_{12}O_8NS_2$, in yellow crystals, m. p. 301° (corr.), which on hydrolysis with concentrated sulphuric acid give *ethylenebis-2-aminoanthraquinone*,



This forms small, orange-yellow crystals, m. p. 400° , and gives a red vat with sodium hyposulphite, cotton being dyed orange.

Fuming sulphuric acid (18–20% SO_3) converts 2-aminoanthraquinone into 2-aminoanthraquinone-3-sulphonic acid, $C_{14}H_9O_3NS$, a faintly yellow powder, which forms a white sulphate by the addition of water to the red solution in concentrated sulphuric acid, and also a golden-yellow sodium salt. Its constitution is determined by the formation of Scholl's 1:3-dibromo-2-aminoanthraquinone [A., 1907, i, 541, m. p. 249.5° (corr.), and not 239°] under the influence of bromine water, and the transformation into 2-chloroanthraquinone by eliminating the amino-group and then replacing the sulphonic group through the medium of sodium chlorate and hydrochloric acid.

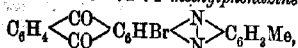
The chief product of the nitration of 2-acetylaminoanthraquinone is 1-nitro-2-acetylaminoanthraquinone, $C_{16}H_{10}O_3N_2$, which forms long, silvery needles, m. p. $277-278^{\circ}$ (corr.), and is hydrolysed by warm concentrated sulphuric acid to 1-nitro-2-aminoanthraquinone, m. p. 310° (corr.) (Terres, this vol., i, 738, gives m. p. 267°). Bayer & Co. (A., 1906, i, 677) also obtained the latter compound by nitrating the carbamate of 2-aminoanthraquinone, m. p. $279-280^{\circ}$, and hydrolysing the carbamate of 1-nitro-2-aminoanthraquinone, m. p. 205° . The addition of glacial acetic acid to the solution in fuming nitric acid, however, precipitates the isomeric carbamate of 3-nitro-2-aminoanthraquinone, $C_{17}H_{12}O_6N_2$, in faintly yellow needles, m. p. 225° (corr.), thus affording a means of obtaining 3-nitro-2-aminoanthraquinone (Scholl, A., 1905, i, 70). When the 1-nitroamine or the urethane is reduced with sodium sulphide, 1:2-diaminoanthraquinone is obtained, m. p. $303-304^{\circ}$



(compare Terres, *loc. cit.*). Reduction of the acetylated base, however, gives rise to 2-methyl-a-anthraquinoneiminazole (annexed formula). This crystallises in yellow leaflets, m. p. 326° (corr.), which form a colourless hydrochloride and an orange-red sodium salt.

1:3-Dibromo-2-aminoanthraquinone condenses with *p*-toluidine in presence of anhydrous potassium acetate to form 3-bromo-2-amino-1-toluidinoanthraquinone, $C_{21}H_{15}O_2N_2Br$, in long, dark red, sparkling needles, m. p. 181° (corr.), which on oxidation with lead peroxide yields

3-bromoanthraquinone-1:2:1':2':4'-methylphenazine,



in pale brown needles, m. p. 247° (corr.). The dye gives a blue hyposulphite vat which colours cotton light blue, but the shade changes to pale yellow in the air.

J. C. W.

Preparation of Nitroaminoanthraquinones. CHEMISCHE FABRIK GIESSEHEIM-ELEKTRO (D.R.-P. 259432).—When the anthraquinone-nitroamines (A., 1905, i, 447) are treated with mineral acids (such as hydrochloric or phosphoric) they are converted into nitroaminoanthraquinones; thus anthraquinone-1-nitroamine (*loc. cit.*) when left in contact with concentrated sulphuric acid for one hour furnishes a mixture of 1:2- and 1:4-nitroaminoanthraquinones.

Anthraquinone-2-nitroamine prepared by the action of sodium hypochlorite on anthraquinone-2-isodiazoxide yields 1-nitro-2-aminoanthraquinone (A., 1906, i, 677), and this on reduction (by ordinary methods) gives rise to 1:2-diaminoanthraquinone, m. p. 242–244°.

Anthraquinone-1:5-dinitroamine furnishes a mixture of 2:6-dinitro- and 4:8-dinitro-1:5-diaminoanthraquinones, whilst anthraquinone-2:6-dinitroamine gives rise to 1:5-dinitro-2:6-diaminoanthraquinone, brown crystals, m. p. over 300°, which on reduction yields 1:2:5:6-tetra-aminoanthraquinone.

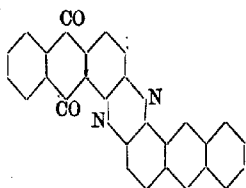
F. M. G. M.

1:2-Diaminoanthraquinone and a Synthesis from it of Indanthrene. ERNST TERRES (*Ber.*, 1913, 46, 1634–1647).—Indanthrene can be obtained from 1:2-diaminoanthraquinone and 1:2-anthraquinone, and the author also describes other angular azines obtained by the interaction of 1:2-diaminoanthraquinone with diethyl oxalate, benzil, 1:2-naphthaquinone, and phenanthraquinone. The two last-named have already been obtained (Farbenfabriken vorm. Friedr. Bayer & Co., A., 1906, i, 905). The nomenclature employed is that proposed in a former paper (Bally and Scholl, *Ber.*, 1911, 44, 1662). The paper also records a reducing action of potassium copper cyanide, which reacts with 2-methylanthraquinonyl-1-diazonium sulphate, yielding 2-methylanthraquinone. The nitrile simultaneously formed is removed by saponifying it to the corresponding acid, which is soluble in water.

In order to exclude the formation of isomeric products, 1:2-diaminoanthraquinone was made (but with poor yield) by a new method, starting from 1-nitro-2-methylanthraquinone. Oxidation of this substance (best effected by concentrated nitric acid and chromic anhydride. Badische Anilin- & Soda-Fabrik, D.R.-P. 228394) yields 1-nitroanthraquinone-2-carboxylic acid, m. p. 283°. On treatment of this acid with sodium sulphide solution on the water-bath, 1-aminoanthraquinone-2-carboxylic acid, $\text{C}_{15}\text{H}_9\text{O}_4\text{N}$, is obtained; it forms brownish-red, shimmering needles, m. p. 286°. When 1-nitroanthraquinone-2-carboxylic acid is boiled for several hours with phosphorus pentachloride in benzene solution, the acid chloride (which crystallises in yellow needles) is produced, and if the reaction mixture is poured into cold alcoholic ammonia solution, the amide, $\text{C}_{15}\text{H}_9\text{O}_5\text{N}_2$, is

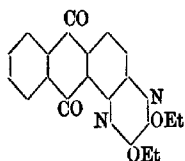
obtained; it forms yellow leaflets or large, almost colourless prisms, m. p. 299—301°. On reduction with ammonium sulphide, the amide yields 1-aminoanthraquinone-2-carboxylamide, $C_{15}H_{10}O_3N_2$, which crystallises in red needles, m. p. 279—281°. 2-Amino-1-nitroanthraquinone, m. p. 266—267° (Farbenfabriken vorm. Friedr. Bayer & Co., A., 1908, i, 677), can be obtained from 1-nitroanthraquinone-2-carboxylic acid by warming it with bromine, potassium hydroxide, and water, but it is necessary that the acid should be freshly precipitated (by pouring an acetic acid solution of it into water). 1:2-Diaminoanthraquinone is obtained by heating 2-amino-1-nitroanthraquinone with ammonium sulphide solution for five hours on the water-bath.

When a mixture of 1:2-diaminoanthraquinone and 1:2-anthraquinone in acetic acid is boiled, transbisanthraquinone



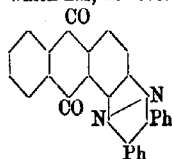
azine (annexed formula) is rapidly deposited as a brownish-red, crystalline paste. It gives a dark green solution in cold, concentrated sulphuric acid, and from this solution water precipitates at first the dark blue sulphate. In concentrated nitric acid the substance dissolves, giving a bluish-green solution, which becomes blue and finally wine-red on warming. Alkali hyposulphite solution

yields an insoluble, bluish-green vat salt. It is possible that the above product contains also the *cis*-isomeride. That the *trans*-form is present is shown by the fact that, by oxidation with chromic acid to anthraquinoneazine and reduction of the latter by means of boiling quinoline, indanthrene is obtainable, although only in very minute quantities and by working in very definite conditions.



Condensation of ethyl oxalate with 1:2-diaminoanthraquinone (by boiling in acetic acid solution) yields 2:3-diethoxyypyrazinoanthraquinone (annexed formula), which crystallises in red needles, m. p. 276—277°. This azine gives a bright yellow solution in sulphuric acid.

With hyposulphite solution it yields a red vat, which has, however, little affinity for unmordanted vegetable fibres.



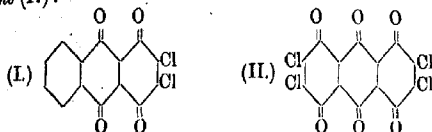
Benzil yields by a similar condensation 2:3-diphenylpyrazinoanthraquinone (annexed formula), which forms yellow needles, m. p. 282—283°. Concentrated sulphuric acid dissolves the substance with production of a dark reddish-brown coloration. Alkali hyposulphite yields a bluish-black, insoluble vat salt.

R. V. S.

Preparation of Anthraquinone Derivatives Containing Halogens. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.P. 258556).—When 1:4-diamino- or 1-amino-4-hydroxy-anthraquinone is treated with chloric acid it furnishes a chlorinated quinone.

1:4-Diaminoanthraquinone (50 parts) dissolved in concentrated sulphuric acid (1000 parts) at 5° is slowly treated during about four hours with finely powdered potassium chlorate (250 parts); the product, a grey powder, crystallises from xylene, contains 23.1% of chlorine, and no nitrogen.

By modifying the reaction, a compound (I) having a higher chlorine content is obtained, and when diaminoanthrarufin (46 parts) with potassium chlorate (450 parts) is employed it gives rise to *tetrachloro-rufinone* (II):



These compounds condense with aromatic amines (eliminating one atom of chlorine), furnishing dyes. F. M. G. M.

[Derivatives of] Some Aromatic Diketones. LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 517—519).—When phenanthraquinone is boiled with an ethereal solution of diazomethane until no more diazomethane remains, nitrogen is evolved, and a substance, $C_{18}H_{10}O_2$, is formed; it crystallises in thin, orange-yellow needles, m. p. 167°. The compound is stable towards permanganate. R. V. S.

The Aliphatic Sequiterpene-Alcohol, Farnesol. MAX KERSCHBAUM (*Ber.*, 1913, 46, 1732—1737).—The author has investigated a number of derivatives of farnesol, an alcohol which is widely distributed in flower-blossom oils (compare A., 1904, i, 513; Soden and Treff, A., 1904, i, 439).

Farnesol, obtained from *Hibiscus Abelsonschus*, L., and purified by the phthalic ester method, has b. p. 160°/10 mm., D_{20}^{25} 0.885, n_D^{20} 1.48809, n_D^{25} $\pm 0^\circ$. It may be preserved in closed vessels for years without alteration. Solid derivatives have not been obtained. The acetate has b. p. 169—170°/10 mm., and is practically odourless. When heated with potassium hydrogen sulphate at 160—170°, farnesol loses water, forming *farnesene*, a colourless, mobile oil, b. p. 129—132°/12 mm., D_{20}^{25} 0.877, n_D^{20} 1.49951, n_D^{25} $\pm 0^\circ$. Oxidation of farnesol by means of chromic acid and dilute sulphuric acid leads to the formation of farnesaldehyde, which, after purification by means of the solid bisulphite compound, has b. p. 172—174°/14 mm., D_{20}^{25} 0.893, n_D^{20} 1.49951, n_D^{25} $\pm 0^\circ$. The corresponding *semicarbazone*, leaflets, m. p. 133—135° after slight previous softening, is well adapted for the identification of farnesol.

Attempts to determine the constitution of farnesol by a study of the products of the action of potassium permanganate on it were not completely successful. Acetone was, however, isolated. When, however, *farnesaldoxime* was converted into the corresponding *nitrile* and the latter saponified by alcoholic sodium hydroxide, *farnesonic acid*, b. p. 202—206°/16 mm., acetic acid, and a ketone were obtained. The latter substance was identified as dihydro- ψ -ionone by

means of its semicarbazone. Since the constitution of the latter follows from its synthesis from geranyl chloride and ethyl sodioacetate followed by saponification of the ethyl geranylacetate by sodium hydroxide, the following formula is ascribed to farnesol: $\text{CMe}_2\text{CH}[\text{CH}_2]_2\text{CMeCH}[\text{CH}_2]_2\text{CMeCHCH}_2\text{OH}$ (compare following abstract).

Dihydro- ψ -ionone is converted by methyl magnesium bromoacetate into a *methyl hydroxydihydrofarnesenate*, which, on prolonged heating with acetic anhydride and sodium acetate at $160-165^\circ$, loses water, and yields *methyl farnesenate*, b. p. $177-185^\circ/10$ mm. The corresponding free acid has a b. p. identical with that of the acid obtained from farnesol. Solid derivatives could not, however, be prepared.

Reduction of methyl farnesenate by sodium and absolute alcohol gives rise to a mixture of dihydro- ψ -ionol, dihydrofarnesol, and, probably, farnesol. The presence of the latter could not, however, be definitely established.

H. W.

Farnesol. CARL HARRIES and REINHOLD HAARMANN (*Ber.*, 1913, 46, 1737-1741).—A study of the action of ozone on farnesol has confirmed the formula ascribed to the latter by Kerschbaum (preceding abstract).

When farnesol is ozonised in hexane solution, a gelatinous *diozonide* is obtained, which, on further treatment with *azone* in chloroform solution, is transformed into the *triozonide*. The latter, when boiled with water, gave the tests for hydrogen peroxide, for the group $\text{C}\cdot\text{CO}\cdot\text{C}\cdot\text{C}\cdot\text{CHO}$ and for aldehydes, whilst acetone, formic and acetic acids, lævulinialdehyde, and lævulinic acid were identified among the products formed.

The action of ozone on farnesene was also investigated, the latter substance having been obtained by the fractionation of a specimen of crude farnesol which had been preserved during several years and which had undergone decomposition to a considerable extent with elimination of water. In carbon tetrachloride solution, the hydrocarbon yields a stable, glassy *tetra-ozonide*, which is decomposed by boiling water with formation of lævulinialdehyde. The latter was identified by conversion into phenylmethyldihydropyridazine, m. p. 197° (Harries, A., 1898, i, 233).

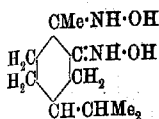
H. W.

Methylcamphoroxime, Methylcampholenitrile, and Methylcampholenic Acid. ALBEN HALLER and ÉDOUARD BAUER (*Compt. rend.*, 1913, 156, 1503-1506).—The mixture of methyl- and dimethyl-camphor obtained by the action of methyl iodide on sodium camphor (compare A., 1909, i, 594) can be separated by the action of hydroxylamine zinc chloride, the methylcamphor being converted into its oxime, m. p. 60° , b. p. $134-135^\circ/11$ mm., $[\alpha]_D^{25} + 25.15^\circ$ (compare Glover, T., 1908, 93, 1285). It gives a *phenylurethane*, prismatic crystals, m. p. $112-113^\circ$, $[\alpha]_D^{25} + 24.8^\circ$, and at the same time a small quantity of slender needles, m. p. $110-111^\circ$, which are inactive. The oxime is hydrolysed by hydrochloric acid into the nitrile, b. p. $105-106^\circ/15$ mm., $[\alpha]_D^{25} + 45^\circ$ (compare Glover, *loc. cit.*). In solution in alcohol it has $[\alpha]_D^{25} + 53.9^\circ$. The nitrile is hydrolysed by

alcoholic potassium hydroxide to methylcamphenamide, m. p. 91—92°, which is completely inactive, and this in its turn is hydrolysed by more concentrated alkali to methylcamphenic acid, m. p. 30°, b. p. 153°/20 mm., which is also inactive. It is probable that the methylcamphenonitrile by reason of its optical activity is analogous to α -camphenonitrile, but in the course of hydrolysis undergoes transformation, its derivatives being of the β -type.

W. G.

*iso*Nitroamines of the Terpenes. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 616—622. Compare Cusmano and Linari, A., 1912, i, 272).—Carvomenthone- $\alpha\beta$ -hydroxylamineoxime (annexed



formula) is obtained by the action of hydroxylamine on carvomenthone bisnitroso-chloride; it forms tufts of long, colourless needles, m. p. 118°. From the mother liquor the following substances can be isolated in small quantity: active carvotanacetoneoxime, oxytetrahydrocarvoneoxime, and two other oximes of m. p. 120° and 160° respectively. The hydroxylamineoxime reduces ammoniacal silver nitrate and Fehling solution. When treated with ferric salts, it yields an amorphous, yellow powder, which is soluble in ether and contains iron. This substance gives Liebermann's reaction, and when shaken in ethereal solution with concentrated hydrochloric acid, it loses its iron, and is converted into a blue compound. The hydroxylamineoxime yields a benzylidene derivative, $\text{C}_{17}\text{H}_{28}\text{O}_2\text{N}_2$, which crystallises in hard, colourless prisms, m. p. 141°. The *p*-nitrobenzylidene derivative is a yellow powder.

Carvomenthone- $\alpha\beta$ -isonitroamineoxime, $\text{C}_{10}\text{H}_{19}\text{O}_2\text{N}_3\cdot\text{H}_2\text{O}$, obtained by the action of sodium nitrite on the hydrochloride of the hydroxylamineoxime above described, forms rectangular tablets, m. p. 64°. It gives blue colorations with sulphuric acid solutions of phenol and diphenylamine. The ammonium and silver salts were prepared. When the aqueous solution of the potassium salt is boiled, the active oxime of carvotanacetone is produced. The *isonitroamineoxime* is fairly stable towards acids; after prolonged boiling with acetic acid or hydrochloric acid only small quantities of tanacetone are formed. When the *isonitroamineoxime* is dissolved in the equimolecular quantity of potassium carbonate and the solution is placed over sulphuric acid, nitrous oxide is evolved, and the salt of oxycarvomenthoneoxime is produced. If this is decomposed with carbonic acid, the oxime, $\text{C}_{10}\text{H}_{18}\text{O}(\text{NOH})$, is obtained in rhomboidal leaflets, m. p. 102°. On evaporating a solution of the oxime in ethyl nitrite the *pernitrosyl* compound is deposited as an oil, and this reacts with semicarbazide to form oxycarvomenthonesemicarbazone, m. p. 172°.

If concentrated methyl-alcoholic solutions of hydroxylamine and 8-*isonitroaminomenthone* are mixed (being cooled meanwhile with ice and salt) the hydroxylammonium salt, $\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}_4\cdot\text{NH}_3\cdot\text{OH}$, is precipitated in long, colourless needles, m. p. 68°. Acids decompose the salt in the cold, yielding the original *isonitroamine*, whilst cold alkalis convert it into pulegone. The salt remains unaltered for a long time in the solid state, but in alcoholic or ethereal solution it is rapidly

transformed into *menthonoisonitroaminoxime*, $C_{10}H_{13}O_2N_2$, which forms large, prismatic crystals, m. p. 77° . This substance gives blue colorations with sulphuric acid solutions of diphenylamine and phenol. It is very stable towards heat, remaining unaltered for a long period at 150° . The *potassium* salt, $C_{10}H_{13}O_2N_2K \cdot 2H_2O$, explodes above 350° . The *sodium* salt, $C_{10}H_{13}O_2N_2Na \cdot 4H_2O$, has m. p. 66° , or when anhydrous, 220° (decomp.). The *ammonium* salt dissociates at about 100° into its components.

R. V. S.

The Constituents of Ethereal Oils. Synthesis of the Diterpene, α -Camphorene, $C_{20}H_{32}$, and of the Sesquiterpene *cycloisoprenemyrcene*, $C_{15}H_{24}$. FRIEDRICH W. SEMMLER and K. G. JONAS (*Ber.*, 1913, 46, 1566—1571. Compare Semmler and Rosenberg, this vol., i, 377).—Unsuccessful attempts have been made to synthesise α -camphorene from isoprene, and also by the addition of two isoprene radicals to limonene.

Myrcene was heated in a sealed tube at 250 — 260° for four hours, and the product subjected to fractional distillation, whereby a portion, b. p. 175 — $195^\circ/8$ mm., was obtained, analyses of which gave results agreeing with the formula $C_{20}H_{32}$. When a cooled, absolute ethereal solution of the product was saturated with dry hydrogen chloride, a crystalline product was obtained identical in all respects with α -camphorene tetrahydrochloride. Successive treatment with glacial acetic acid and sodium acetate, and with alcoholic potassium hydroxide, converted it into α -camphorene identical with the substance obtained from camphor oil of high boiling point, from which the tetrahydrochloride could be regenerated. The mother liquor obtained from the α -camphorene tetrahydrochloride, on treatment with glacial acetic acid and sodium acetate and, subsequently, with alcoholic potassium hydroxide, yielded other diterpenes which appeared to be bicyclic.

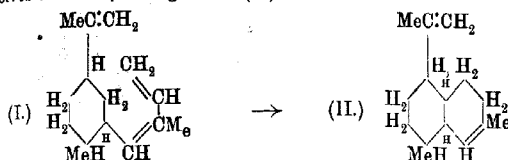
Since myrcene is a butadiene and undergoes condensation when heated, attempts were made to obtain a condensation product from myrcene and isoprene. When these substances were heated in a sealed tube for three and a-half hours at 225° and the product fractionated, the following fractions were obtained: (i) unchanged isoprene; (ii) b. p. 52 — $65^\circ/8$ mm., consisting of dipentene obtained partly from the condensation of two isoprene molecules, and partly by the isomerisation of myrcene; (iii) b. p. 120 — $150^\circ/8$ mm., which, on subsequent distillation, yielded *cycloisoprenemyrcene*, b. p. 125 — $135^\circ/8$ mm., n_D^{20} 1.49166 , n_D^{25} 1.48685 . The latter yielded a *trihydrochloride*, m. p. 83° , from which the hydrocarbon could be regenerated in the usual manner, and again converted into the hydrochloride; (iv) b. p. 175 — $195^\circ/8$ mm., n_D^{20} 1.5034 , n_D^{25} 1.49890 , and (v) a considerable residue.

H. W.

The Constituents of Essential Oils. The Constitution of Zingiberene. Transformation of the Monocyclic Zingiberene into the Bicyclic *iso*Zingiberene. FRIEDRICH W. SEMMLER and A. BECKER (*Ber.*, 1913, 46, 1814—1822).—Of the naturally-occurring monocyclic sesquiterpenes, only limene and zingiberene have been studied. The former can be regenerated from its trihydrochloride, but

the latter gives a dihydrochloride which no longer yields the original oil with alkali. The conclusion is therefore drawn that the hydrochloride contains a different ring system. In addition, the abnormal molecular refraction, 68.37 instead of 67.86, suggests that two of the three unsaturated linkings are adjacent in a side-chain.

Consequently, like myrcene, which has a similar structure and may be reduced to dihydromyrcene and readily transformed into cyclic terpenes, zingiberene (I) may be reduced to dihydrozingiberene and also converted into a bicyclic hydrocarbon. The latter is found to yield the above hydrochloride, from which it may be regenerated. It receives the name, *isozingiberene* (II).



Finally, like other butadienes, zingiberene may be polymerised or condensed with isoprene.

The reduction of zingiberene (b. p. 128—129°/9 mm., D^{20}_D 0.8684, n_D 1.4956) by means of sodium and alcohol results in the formation of monocyclic *dihydrozingiberene*, $C_{15}H_{26}$, with b. p. 122—125°/7 mm., D^{20}_D 0.8557, n_D 1.4837, $[\alpha]_D - 37^\circ$. The complete reduction with platinum and hydrogen yields monocyclic *hexahydrozingiberene*, $C_{15}H_{30}$, with b. p. 128—130°/11 mm., D^{20}_D 0.8264, n_D 1.4560, $[\alpha]_D - 10^\circ 12'$. The linking-up of the side-chain into a ring is effected by dissolving the zingiberene in glacial acetic acid containing a small amount of sulphuric acid, and agitating for some hours at 60—65°. *isoZingiberene*, $C_{15}H_{24}$, yields the same chloride as zingiberene itself (Schreiner and Kremers, A., 1902, i, 108) and also a *dihydrobromide*, m. p. 175°, from which alcoholic potassium hydroxide regenerates the pure hydrocarbon, with b. p. 120—123°/8 mm., D^{20}_D 0.9150, n_D 1.5034, $[\alpha]_D - 41^\circ$. Reduction with platinum and hydrogen converts the substance into *tetrahydroisozingiberene*, $C_{15}H_{28}$, which is similar to other bicyclic tetrahydrosesquiterpenes, and has b. p. 123—123.5°/10 mm., D^{20}_D 0.8822, n_D 1.4791, and $[\alpha]_D + 4^\circ 36'$.

When heated with isoprene in a sealed tube, zingiberene gave a mixture which was fractionated, and found to contain i-limonene, a bicyclic, dextrorotatory, modified zingiberene, "meta-zingiberene," a diterpene from the condensation of isoprene with zingiberene, and dizingiberene.

J. C. W.

[Essential Oils.] SCHIMMEL & Co. (*Semi-Annual Report*, April, 1913, pp. 20—153. Compare A., 1912, i, 880).—First runnings from the distillation waters of angelica contained methyl alcohol, ethyl alcohol, furaldehyde, diacetyl, and a base having an odour of pyridine.

Angostura bark (*Cusparia trifoliata*, Eng.) yielded 1.03% of oil, D^{20}_D 0.9285, $n_D^{20} - 7^\circ 32'$, n_D^{20} 1.50744, of pale brown colour and having

acid number 1.8, ester number 5.5, acetyl ester number 35.7; the oil is not completely soluble even in 9 vols. of 90% alcohol.

Arnica root oil, D_{15}^{20} 0.984—1.00, $n_D^{20} + 0.25' - 2''$, n_D^{20} 1.507—1.508, had acid number 4 to 10, ester number 60 to 100, and gives a turbid solution with 7 to 12 vols. of 80% or 0.5 to 6.0 vols. of 90% alcohol. Arnica flower oil, D_{20}^{20} 0.8905 to 0.9029, acid number 62.6 to 127.3, ester number 22.7 to 32.2, is a buttery mass, m. p. 20—30° (approx.), and very sparingly soluble in alcohol.

Artemisia vulgaris, L., oil from India, had D_{15}^{20} 0.9219, $n_D^{20} - 8.53'$, n_D^{20} 1.46201, acid number 1.2, ester number 22.1, acetyl ester number 55.5, and was soluble in 1 vol. of 80% alcohol, becoming turbid and depositing crystals of a solid paraffin on further dilution. The oil was of greenish-yellow colour and sage-like odour. It contains α -thujone, and possibly borneol.

Banana fruit oil according to Kleber (*Amer. Perf.*, 1912, 7, 235) contains amyl acetate and traces of a phenol.

Borneo camphor oil, D_{15}^{20} 0.9180, $n_D^{20} + 11.5'$, n_D^{20} 1.48847, was of dark brown colour, soluble in 5 vols. or more of 90% alcohol, and had acid number 5.6, ester number 0, acetyl ester number 50.5. It contained α -pinene, β -pinene, dipentene, and camphene (35% of terpenes in all), borneol, and α -terpineol (10% together), sesquiterpenes 20%, and resin 35%.

The "Camphor leaf oil" (*Cinnamomum camphora*) described previously (A., 1905, i, 537) is now stated to be from the leaves of *Cinnamomum glanduliferum*, Meissn. It contains no camphor (compare Pickles, T., 1912, 101, 1433). An oil from a hybrid between these two species deposited 58% camphor on freezing, and then had D_{15}^{20} 1.0465, $n_D^{20} + 34.24'$, acid number 1.0, ester number 23.3, acetyl ester number 46.2, and was soluble in 0.8 vol. of 80% alcohol. It still contained camphor, but no safrole could be detected.

Further investigation of Seychelles cinnamon bark oil (A., 1909, i, 112) shows that it contains the same constituents as Ceylon cinnamon bark oil.

The comparison of various methods for the estimation of geraniol and citronellal in citronella oils has been continued (A., 1912, i, 880). Kleber's phenylhydrazine process gives the following percentage values: *Java oil*, citronellal 35—41.3, geraniol 26.6—40.1; *Ceylon oil*, citronellal 7.5—11.6, and geraniol 29.6—34.4. Dupont and Labaune's method gives citronellal 35.4—46.3% and 6.5—8.0% for Java and Ceylon oils respectively. Kleber's phenylhydrazine process may also be used for cuminaldehyde, benzaldehyde, and methyl nonyl ketone; in the case of oil of bitter almonds only the free benzaldehyde reacts with phenylhydrazine. The process is being tried for the estimation of ketones in rue oil.

The two alcohols already noticed in cypress oil (A., 1904, i, 604) have been further examined: the chief constituent of the mixture is now shown to be 4-terpineol; the second alcohol, $C_{10}H_{18}O$, has D_{15}^{20} 0.9422, $n_D^{20} + 43.38'$, n_D^{20} 1.46678, b. p. 76—77°/4—5 mm., and has a rose odour with a suggestion of borneol. The highest fractions of the oil contain in addition to cypress camphor and cadinene, a liquid

sesquiterpene alcohol, $C_{15}H_{20}O$, b. p. $136-138^{\circ}/4-5$ mm., which on treatment with formic acid yields a hydrocarbon.

Dipterocarpus turbinatus, Gaertn., oleo-resin yielded 46% of a pale yellow balsamic oil, D_{15}^{20} 0.9271, α_D^{20} -37° , n_D^{20} 1.50070, acid number 0, ester number 1.9, soluble in 7 vols. of 95% alcohol. *D. tuberculatus*, Roxb., oleo-resin gave 33% of a yellowish-brown oil, D_{15}^{20} 0.9001, α_D^{20} $-99^{\circ}40'$, n_D^{20} 1.50070, soluble in 6 vols. of 95% alcohol. Both these oleo-resins and oils gave Turner's colour reaction.

Caryophyllene was detected in a French lavender oil.

Lemon-grass oils from Assam, Burma, Formosa, Celebes, and Mayotte are described: these are mostly of the "insoluble" type.

Mentha aquatica, L., herb yielded 0.8% of oil, D_{15}^{20} 0.9553, α_D^{20} $+64^{\circ}56'$, n_D^{20} 1.48276, of pale yellow colour and having a faint odour of mint. *Mentha sylvestris*, L., herb gave 0.9% of similar oil, D_{15}^{20} 0.9852, α_D^{20} $-132^{\circ}52'$, n_D^{20} 1.46856. *M. viridis* herb gave 0.17% of oil, D_{15}^{20} 0.9512, α_D^{20} $-52^{\circ}5'$.

Mosla Japonica, Max.* oil according to Nurayama and Nara (*J. pharm. Soc. Japan*, 1912) contains α -pinene (compare A., 1910, i, 328).

Coclea pretiosa, Benth., bark gave 0.83% of a brown oil, D_{15}^{20} 1.1200, n_D^{20} 1.52712, soluble in 6.5 vols. of 88% alcohol, and having a cinnamon-like odour. The oil is nitrogenous, contains no cinnamaldehyde, but probably contains caryophyllene, phenols, and lactones.

d-Ethyl-*n*-amylcarbinol from Japanese peppermint oil (A., 1912, i, 370) yields a benzoate, D_{15}^{20} 0.9641, α_D^{20} $+5^{\circ}58'$, n_D^{20} 1.48905, b. p. $126.5^{\circ}/3$ mm., which is viscous, colourless, and possesses a faint odour. The acetate, D_{15}^{20} 0.8693, α_D^{20} $-4^{\circ}46'$, n_D^{20} 1.41535, b. p. $194-194.5^{\circ}/760$ mm., has a peculiar odour of fruit and roses. The inactive modification of the alcohol, D_{15}^{20} 0.8286, n_D^{20} 1.42785, b. p. $176-177.5^{\circ}$, has been synthesised by the action of magnesium ethyl iodide on *n*-hexaldehyde.

Rhus Cotinus, L., leaves and flowers yielded a very pale yellow oil, D_{15}^{20} 0.8710, α_D^{20} $+32^{\circ}54'$, n_D^{20} 1.4887, acid number 0.9, ester number 20.4, soluble in 6 vols. 90% alcohol, and having an odour of terpenes, but slightly suggestive of neroli; it contained camphene, β -pinene (β), and limonene; no phellandrene or terpinene could be detected.

Amomum globosum fruits ("wild cardamoms") from Indo-China yielded 4% of a colourless oil, D_{15}^{20} 0.9455, α_D^{20} $+43^{\circ}54'$, n_D^{20} 1.47141, acid number 0.8, ester number 128.4, insoluble in 10 vols. of 70% alcohol, but soluble in 1 vol. of 80% alcohol and having a strong odour of camphor.

Cherry stones when ground and left for several hours furnished, on steam distillation, 0.016% of an oil, D_{15}^{20} 1.0532, α_D^{20} 0° , n_D^{20} 1.53888, soluble in 2.5 vols. of 60% alcohol, having an odour similar to, but clearly different from, that of bitter almond oil, and containing 0.27% of hydrocyanic acid.

Fennel herb from Jersey yielded an oil, D_{15}^{20} 0.9561, α_D^{20} $+16^{\circ}40'$, soluble in 5 vols. 80% alcohol. Its odour indicated that methyl-chavicol was the chief constituent, and that very little anethole was present.

Meum athamanticum, Jacq., herb from the Harz mountains yielded

0.88% of a deep reddish-brown oil, D_4^{20} 0.9053, n_D^{20} 1.50327, acid number 8.8, ester number 63.1, soluble in 3 vols. of 90% alcohol, which had a celery-like odour, and on keeping deposited crystals, m. p. 91° (guaiacol?).

The Report also contains a résumé of recent work on the chemistry, pharmacology, etc., of essential oils and their constituents.

T. A. H.

[Essential Oils.] ROURE-BERTRAND FILS (*Sci. Ind. Bull.*, 1912, [iii], 6, 3—191; 1913, [iii], 7, 3—147).—*Calamintha Nepeta*, Lk. and Hoff., grown in Sicily, yielded 0.1426% of a brown oil, D_4^{20} 0.9249, n_D^{20} +17.48, acid number 1.4, saponification number 12.6, which has an odour of pennyroyal, is soluble in 0.5 or more vols. of 80% alcohol, contains 20% of pulegone and 14% of alcohols, with a considerable quantity of a second ketone (menthone?).

Lemon grass oils from Mayotte, distilled from *Cymbopogon citratus*, had D_4^{20} 0.8877—0.9072, n_D^{20} -0.4'—0.6', aldehydes 75.5 to 78% and were insoluble in 90% alcohol.

Basil oils from Mayotte had D_4^{20} 0.9630—0.9677, n_D^{20} +0.56'—0.58', acid number 0.7 to 1.4, saponification number 5.6 to 6.3, esters 1.9 to 2.2%, and were soluble in 3.0 to 3.2 or more vols. of 80% alcohol. These oils had an odour of anethole as well as of estragol.

[JUSTIN DUPONT and LOUIS LABAUNE.]—With a view to ascertaining the cause of the anomalous results obtained in estimating aldehydes in essential oils by means of sodium hydrogen sulphite solution, the authors have investigated the action of such solutions on a large number of common unsaturated constituents of essential oils and find that many of these are wholly or partly converted into hydro-sulphonates when shaken for some time with aqueous solutions of sodium hydrogen sulphite. Among the unsaturated substances which do not react in this way are hydrocarbons (for example, *l*-pinene, limonene, and styrene), esters, ethers, isoeugenol, and ionones. The results with all the substances examined are tabulated in the original. The following were isolated, the sodium hydrogen sulphite compounds of geraniol $C_{10}H_{18}O_2 \cdot 2NaHSO_3$; linalool, $C_{10}H_{18}O_2 \cdot 2NaHSO_3$; terpineol, $C_{10}H_{18}O_2 \cdot NaHSO_3$; methylheptenone, $C_8H_{14}O \cdot NaHSO_3$; they are all hygroscopic masses (compare Labbe, A., 1900, i, 149), and are stable, since they do not regenerate the original organic constituent on addition of alkali. In a second paper on the analysis of citronella oil the authors point out that in Boule's method for the assay of this oil (A., 1912, ii, 1105; Schimmel & Co., A., 1912, i, 880), the results for citronellal are liable to be rendered inaccurate by the absorption of a larger or smaller portion of the geraniol in the hydrogen sulphite solution.

Both "Bulletins" contain summaries of work recently published on essential oils.

T. A. H.

Theory of the Vulcanisation of Caoutchouc. II. GUSTAV BERNSTEIN (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 273—277. Compare A., 1912, ii, 1007).—A continuation of the discussion of the theory of vulcanisation. It is shown that before vulcanisation occurs

a depolymerisation of the caoutchouc must take place, and that at the same time a polymerisation of the sulphur occurs. These two changes are shown to take place under the same conditions, whether the vulcanisation is effected by heat or by ultra-violet light. It is stated that the absorption of sulphur begins only when it has been converted into the insoluble form. It is also stated that the physical properties of the vulcanised product depend on the condition of aggregation of the caoutchouc at the moment of the formation and absorption of the insoluble sulphur.

J. F. S.

Biochemical Synthesis of Alkylglucosides (α -Glucosides) by means of a Ferment (α -Glucosidase) contained in Air-dried, Bottom Yeast: α -Propylglucoside and α -Allylglucoside. ÉMILE BOURQUELOT, HENRI HÉRISSEY, and MARC BRIDEL (*Compt. rend.*, 1913, 156, 1493—1495; *J. Pharm. Chim.*, 1913, [vii], 7, 525—529. Compare this vol., i, 323, 428).— α -Propylglucoside, crystallising in long needles, having a bitter taste, $[\alpha]_D + 140.8^\circ$, and α -allylglucoside, colourless needles, m. p. $85-90^\circ$, $[\alpha]_D + 131.72^\circ$, are obtained by the action of α -glucosidase on solutions of dextrose in water containing 15% of the respective alcohols. They are, both very soluble in water, and are readily hydrolysed in aqueous solution by the above ferment.

W. G.

Biochemical Synthesis, by means of Emulsin, of a Glucoside Isomeric with Salicin, β -Salicylglucoside. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1913, 156, 1790—1792).—Emulsin acts on a solution of salicyl alcohol and dextrose in acetone, containing 20% water, giving β -salicylglucoside, which is finally obtained crystallising in long, colourless needles, $[\alpha]_D - 37.5^\circ$, the melting point varying considerably with the rate of heating. It is odourless, but possesses a bitter taste and is soluble in water, crystallising with $4H_2O$. It reduces Fehling's solution and gives a violet colour with ferric chloride, which does not disappear on shaking with ether. The yield of glucoside varies with the dilution of the acetone and the amounts of alcohol and dextrose used, the presence of an excess of alcohol favouring the synthesis. The glucoside is readily hydrolysed in aqueous solution by emulsin.

W. G.

Cerebrosides of the Brain. III. HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1913, 85, 35—58. Compare Loening and Thierfelder A., 1911, i, 898; 1912, i, 372).—Prolonged treatment of cerebrone with barium hydroxide is shown not to produce any marked change. The cerebrone fraction is found to consist of a crystalline and an amorphous component which have the same composition and optical rotatory power, but differ in solubility. The name cerebrone is retained for the crystalline substance and that of phrenosin restricted to the amorphous form. In addition to the cerebrone fraction the use of a mixture of chloroform and methyl alcohol as solvent resolves the mixed cerebrosides into a very soluble fraction and a fraction of intermediate solubility to which the term kerasin is applied. Acid hydrolysis of

this fraction shows it to be broadly similar to cerebrone. It yields about 20% of galactose, some quantity of dimethylsphingosine as sulphate, and *keratinic acid*, $C_{24}H_{48}O_2$, which crystallises in slender, long needles, m. p. 77—78°.

E. F. A.

New Derivatives of Artemisin and Santonin. ENRICO RIMINI and TEMISTOCLE JONA (*Chem. Zentr.*, 1913, i, 1773; *from Rend. Soc. Chim. Ital.*, 1913, 5, ii, 52—53. Compare Weinhaus and Oettingen, this vol., i, 474, and Wedekind and Beniers, this vol., i, 476).—These substances have been reduced by Paal's method. *Tetrahydroartemisin*, $C_{15}H_{22}O_4$, forms lustrous leaflets, m. p. 192—193°, and tetrahydro-santonin has m. p. 153—155°. Both compounds are stable towards permanganate.

J. C. W.

"Tecomin." OTTO A. OESTERLE (*Arch. Pharm.*, 1913, 251, 301—303).—The colouring matter described under this name by Lee (T., 1901, 79, 284) as occurring in the wood of *Bignonia tecoma* (Ipé wood or Ipé-tabaco wood) is now shown to be lapachol. The latter also occurs in the timbers of *Tecoma Ipé*, Mart. (Ipé preto), and *Tecoma ochracea* (Ipé amarillo), but not in greenheart wood, derived from *Nectandra Rodiaei*. The usual source of lapachol is "Surinam greenheart" derived from *Bignonia leucozydon* (compare Stein, *Jahresb.*, 1866, 651).

T. A. H.

[Bilirubic Acid and Derived Substances.] HANS FISCHER (*Ber.*, 1913, 46, 1574—1577. Compare Piloty, this vol., i, 500).—Polemical. In regard to disputed questions of nomenclature, the author's proposals are as follow: (1) the acid $C_{17}H_{24}O_8N_2$ (Fischer and Röse, A., 1912, i, 575) is bilirubic acid; (2) the acid $C_6H_{10}O_5N$ (Piloty and Thannhauser, A., 1912, i, 736) is isophonopyrrolecarboxylic acid; (3) if, as is probable, xanthobilirubic acid is identical with Piloty's dehydrobilirubic acid (dehydrobilic acid, Piloty and Thannhauser, A., 1912, i, 925), then the latter name should be adopted. R. V. S.

Constitution of Lutein. CESARE SERONO (*Chem. Zentr.*, 1913, i, 1198; *from Arch. Pharmacol. Experim.*, 1912, 14, 509—511. Compare A., 1911, ii, 1005).—The opinion expressed by Willstätter and Escher that lutein from the yolks of eggs is a xanthophyll (A., 1912, i, 125) cannot be reconciled with that of the author who believes it to be an ethereal combination of cholesterol with unsaturated fatty acids.

J. C. W.

Angostura Alkaloids. Decomposition Experiments with Cusparine. JULIUS TRÖGER and W. BECK (*Arch. Pharm.*, 1913, 251, 246—290. Compare A., 1912, i, 895).—Further analyses of cusparine and of its derivatives show that this alkaloid has the formula $C_{10}H_{17}O_3N$ (compare Körner and Böhringer, A., 1884, 341, and Tröger and Muller, A., 1910, i, 414). Further descriptions of the purification of this alkaloid and of the isolation of galipoidine and of a new alkaloid are given.

Cusparine, $C_{19}H_{17}O_3N$, appears to be trimorphic, since in addition

to the two forms already described (*loc. cit.*, and A., 1911, i, 482) a third crystallising in long, pale yellow needles, m. p. 91—92°, was obtained by slow crystallisation from light petroleum. The oxalate, $B_2C_4H_6O_4 \cdot \frac{1}{2}H_2O$, m. p. 140—150°, crystallises in sulphur-yellow needles from water and is efflorescent. The *succinate*, $B_2C_4H_6O_4 \cdot \frac{1}{2}H_2O$, m. p. 80°, crystallises in greenish-yellow needles, loses water on standing in a desiccator and becomes anhydrous and colourless when crystallised from alcohol and then melts at 113°. The *malate*, $B_2C_4H_6O_5$, m. p. 152°, forms heavy, prismatic crystals from water. The *tartrate*, $B_2C_4H_6O_6 \cdot H_2O$, m. p. 161—162°, forms yellow, microscopic crystals from water. The *citrate*, $B_2C_6H_8O_7$, m. p. 174° (decomp.), crystallises in long, sulphur-yellow, prismatic needles. All these organic salts on melting yield pyro-cusparine, $C_{16}H_{13}O_5N$, m. p. 255°, which crystallises from alcohol in masses of slender, colourless needles (compare Beckurts and Frerichs, A., 1904, i, 84), and yields well-crystallised salts: *hydrochloride*, $BHCl$, m. p. 207°, stellate groups of colourless needles; *platinichloride*, $B_2H_2PtCl_6$, m. p. above 150° (decomp.), reddish-yellow, glancing needles. Cusparine methiodide, m. p. 190°, yellow prisms; *ethiodide*, m. p. 206—212°, yellowish-brown, prismatic crystals, and the *n-propyl iodide*, m. p. 187° (decomp.), yellow prisms, were prepared. These on treatment with silver hydroxide or potassium hydroxide do not yield as Beckurts supposed (A., 1896, i, 66) the corresponding alkylcusparines, but the same *isomeride* of cusparine, m. p. 194°, crystallising from alcohol in colourless, prismatic needles, containing water of crystallisation, which is lost at 105°. This substance yields a *platinichloride*, m. p. 185° (approx.), crystallising in microscopic needles and with nitric acid yields a *nitro*-compound, $C_{16}H_{16}O_5N_2$, m. p. 234—235°, which forms greenish-yellow crystals from alcohol. Cusparine is optically inactive, does not react with hydroxylamine, yields no definite products when treated with acids or alkalis in closed vessels at 100° and in common with pyro-cusparine and "nitro-cusparine" (Tröger and Runne, A., 1911, i, 482) contains no $\cdot OH$ group. When heated for several days at 100° with nitric acid ($D = 1.075$), cusparine yields an *acid*, $C_{10}H_7O_5N \cdot H_2O$, m. p. 271—272°, which is probably a hydroxyquinolinecarboxylic acid, since on heating at 300° it loses carbon dioxide and furnishes a *base* from which a *platinichloride*, $(C_9H_7ON)_2 \cdot H_2PtCl_6 \cdot 2H_2O$, m. p. 220° (decomp.), forming yellowish-red crystals, was obtained. On distillation over zinc dust the acid yielded quinoline (identified by means of the platinichloride). On the basis of these results a skeleton-formula for cusparine is suggested.

When galipoidine is examined by Zeisel's method it yields less methyl iodide than is required for $\cdot OCH_3$ in the formula $C_{15}H_{15}O_4N$ (A., 1911, i, 482).

In the purification of cusparine a fourth *alkaloid*, $C_{16}H_{13}O_5N$ (i), m. p. 186°, crystallising from boiling alcohol in sulphur-yellow, rhombic crystals was obtained.

T. A. H.

Carpiline or Pilosine. ÉMILE LÉGER and FERDINAND ROQUES (*Compt. rend.*, 1913, 156, 1687—1689).—The two bases, one soluble and the other insoluble in water, obtained by heating carpiline with

water in a sealed tube at 140° for ten hours (compare this vol., i, 83), are shown to be identical with the pilosinine and anhydriposinine of Pyman (compare T., 1912, 101, 2260). W. G.

Ephedrine. ERNST SCHMIDT (*Arch. Pharm.*, 1913, 251, 320).—It is shown that the asymmetry of ephedrine and ψ -ephedrine cannot be solely dependent on the $\cdot\text{CH}(\text{OH})\cdot$ group, since the conversion of this into a $\cdot\text{CH}_2\cdot$ group does not destroy the optical activity.

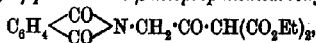
A base, $\text{C}_{10}\text{H}_{15}\text{N}$ (hydrochloride has $[\alpha]_D + 19.14^\circ$), has been prepared by treating ephedrine hydrochloride with phosphorus pentabromide and reducing the bromide, $\text{C}_{10}\text{H}_{14}\text{NBr}\cdot\text{HBr}$ (glistening leaflets), with zinc and hydrochloric acid. This bromide on treatment with silver nitrate does not regenerate ephedrine, but gives ψ -ephedrine, m. p. 117° , $[\alpha]_D + 49.45^\circ$ (compare A., 1912, i, 644). The optical activity of the base $\text{C}_{10}\text{H}_{15}\text{N}$ must be due to the $\cdot\text{CHNMe}$ group (compare Emde, A., 1909, i, 77; Gadamer, *ibid.*, i, 49), which, moreover, cannot be situated at the end of the C_3H_7 chain. T. A. H.

The Homologues of Morphine, Codeine and Dionine, and Some of their Derivatives. FRIEDRICH FERREIN (*Chem. Zentr.*, 1913, i, 1696—1698).—Attempts have been made to prepare a hydroxycodeine by the elimination of the amino-group from aminocodeine and to obtain nitroethyl- and aminoethyl-morphine: Vongerichten and Weilinger (A., 1905, i, 542) obtained diacetylaminocodeine by the reduction of nitrocodeine with tin and acetic acid, whereas the *mono*-derivative, $\text{C}_{20}\text{H}_{24}\text{O}_4\text{N}_2$, has now been obtained by the same method. It yields a hydrochloride and a sulphate, and also *acetylaminocodeine methiodide*, $\text{C}_{21}\text{H}_{27}\text{O}_4\text{N}_2\text{I}$, as a white substance, m. p. $215\text{--}216^\circ$, which is converted into triacetylaminomethylmorphol (*ibid.*) on heating with acetic anhydride and silver acetate. When nitrocodeine is reduced by stannous chloride, however, the product is *aminocodeine*, $\text{C}_{18}\text{H}_{22}\text{O}_3\text{N}_2$, which forms pale yellow crystals, m. p. 224° , and gives what is probably a hydroxy-compound on diazotising and warming.

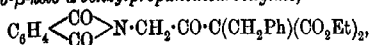
Ethylmorphine (dionine) has also been nitrated. *Nitroethylmorphine*, $\text{C}_{19}\text{H}_{23}\text{O}_5\text{N}_2$, forms yellow crystals, m. p. $166\text{--}167^\circ$; *aminoethylmorphine*, obtained by reduction with stannous chloride, has m. p. $115\text{--}116^\circ$; *acetylaminooethylmorphine*, by reduction with tin and acetic acid, forms a pale yellow hydrochloride; and *diacetylaminooethylmorphine*, $\text{C}_{23}\text{H}_{28}\text{O}_5\text{N}_2$, prepared by acetylating the amino-compound, has m. p. 156° .

All these substances give very similar reactions with formaldehyde-sulphuric acid, Froehde's and Erdmann's reagents. J. C. W.

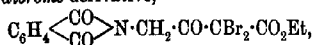
Action of Acylamino-acid Chlorides on Ethyl and Methyl Sodiomalonnate and Ethyl Sodiocyanacetate. II. ERNST PRAHLER (*Ber.*, 1913, 46, 1702—1716. Compare this vol., i, 622).—A mixture of a benzene solution of phthalylglycyl chloride with ethyl sodiomalonate (compare Gabriel and Colman, A., 1909, i, 491) gives a clear liquid from which during several days there separates the sodium derivative of ethyl γ -phthalimino- β -ketopropanedicarboxylate,



prisms, m. p. 68—68.5°; this ester with an alcoholic solution of sodium ethoxide yields needles of the sodium derivative, whilst it dissolves in aqueous ammonia solution shortly depositing the ammonium derivative, decomp. at 210°, m. p. 255—260°; it has an acid reaction, and gives a deep red coloration with ferric chloride in alcoholic solution; in chloroform solution it reacts with bromine, forming a bromo-derivative, $C_{17}H_{15}O_5NBr$, needles, m. p. 122—123.5°, whilst the corresponding chloro-compound forms needles, m. p. 95—96°. The sodium derivative when boiled with water and the solution acidified yields phthalylglycine, whilst the ketonic acid is decomposed by boiling with concentrated hydrochloric acid with the production of amino-acetone hydrochloride. When heated for six hours at 185° with benzyl chloride, the sodium derivative is converted into ethyl γ -phthalimino- β -keto- α -benzylpropanedicarboxylate,

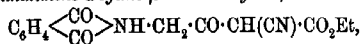


cubes, m. p. 98°. The free ester, ethyl phthalylglycylmalonate, when warmed with water at 100°, undergoes hydrolysis with subsequent loss of a molecule of carbon dioxide, giving rise to ethyl γ -phthaliminoacetoacetate, m. p. 110°; this gave a coloration with ferric chloride, but no metallic derivatives could be isolated; the $\alpha\alpha$ -dibromo-derivative,



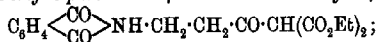
m. p. 87—88°, was obtained by direct substitution in chloroform solution.

Phthalylglycyl chloride in benzene solution readily reacts with a bimolecular proportion of ethyl sodiocyanoacetate; the sodium derivative which separates, on treatment with hydrochloric acid, yields the free ethyl γ -phthalimino- α -cyano- β -keto- n -butyrate,



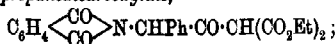
needles, m. p. 148—149°; on boiling with water, this substance undergoes considerable change, and after a few hours pure phthalic acid is obtained.

The clear liquid, obtained by mixing ethyl sodiomalonate and phthalyl- β -alanyl chloride in benzene slowly deposits the sodium derivative of ethyl δ -phthalimino- β -ketobutanedicarboxylate,



the free ester, needles, m. p. 68—69°, can be liberated by hydrochloric acid; it is a strongly acidic substance, which with ferric chloride gives a red coloration, and when boiled with water yields ethyl δ -phthalimino- β -keto- n -valerate, m. p. 121—122°.

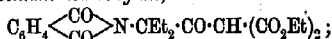
Phthalylphenylglycyl chloride, m. p. 141—143°, was prepared by treating the acid with phosphorus pentachloride; its interaction with ethyl sodiomalonate yielded the sodium derivative of ethyl γ -phthalimino- β -keto- γ -phenylpropanedicarboxylate,



the free ester, leaflets and prisms, m. p. 104—105°, is acid in reaction,

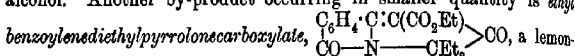
and gives red colour with ferric chloride; when boiled with a mixture of concentrated hydrochloric acid and acetic acid it undergoes scission, producing α -aminobenzyl methyl ketone.

α -Phthalimino- α -ethyl-*n*-butyryl chloride and ethyl sodiomalonate give as reaction product the yellow sodium salt of *ethyl γ -phthalimino- β -keto- γ -ethyl-*n*-pentanedicarboxylate*,



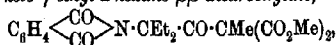
the free ester, prisms, m. p. 72–73°, gives the ferric chloride reaction, but is not appreciably acidic; unlike the esters described above, when warmed with sodium ethoxide, it undergoes rearrangement, yielding an acid substance, which from analogy with the corresponding *gem*-dimethyl compound (Pfahler, *loc. cit.*) is probably a pyrrolidone derivative of the structure $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{N} \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{CH} \cdot \text{CO}_2\text{Et}$. In the original

preparation, involving the acid chloride and ethyl sodiomalonate, the sodium derivative produced is accompanied by a substance, cubical crystals, m. p. 229–230°, insoluble in water, which proves to be α -phthalimino- α -ethyl-*n*-butyric anhydride, a remarkably stable substance, which is not affected by phosphorus pentachloride or boiling water or alcohol. Another by-product occurring in smaller quantity is *ethyl benzoylenediethylpyrrolonecarboxylate*,



yellow substance, m. p. 85–85.5°, which is obtained in larger quantity if the reaction mixture is kept for a longer time under benzene containing an additional quantity of ethyl sodiomalonate. The normal ester, m. p. 72–73°, when boiled for thirty minutes with hydriodic acid (b. p. 127°) undergoes scission, yielding *methyl α -amino- α -ethyl-*n*-propyl ketone hydriodide*, short, columnar crystals, m. p. 184–186°; *hydrochloride*, silky needles, m. p. 236–236.5°; *platinochloride*, lemon-yellow needles, m. p. 188° (decomp.); *picrate*, yellow needles, m. p. 166°; *benzoyl* derivative, needles, m. p. 80–81°; the free base has an odour resembling that of turpentine.

Methyl sodiomalonate behaves like the corresponding ethyl compound towards phthaliminoethylbutyryl chloride, producing as by-product the same acid anhydride as mentioned above, together with the sodium derivative of *methyl γ -phthalimino- β -keto- γ -ethyl-*n*-pentanedicarboxylate* as main product; the free ester, prisms, m. p. 97–98°, is neutral, but gives the ferric chloride reaction; with sodium ethoxide it shows the same behaviour as the ethyl ester, whilst its sodium derivative when heated with methyl iodide in acetone solution is converted into *methyl δ -phthalimino- γ -keto- γ -ethyl-*n*-hexane- $\beta\beta$ -dicarboxylate*,



needles, m. p. 113–114°, which gives no ferric chloride reaction. Again, like the ethyl ester, the methyl ester in benzene solution is converted by the action of methyl sodiomalonate into *methyl benzoylenediethylpyrrolonecarboxylate*, lemon-yellow needles, m. p. 109–110°; this and also the corresponding ethyl ester are converted by hydrobromic acid into

diethylpyrrolonebenzoic acid hydrobromide, yellow cubes, m. p. 214° (decomp.), which by the action of water or alkali yields *diethylpyrrolonebenzoic acid*,

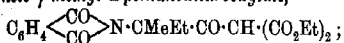
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{NH} \\ \text{CO} \text{---} \text{CH} \end{array} > \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}, \text{ prisms and leaflets,}$$

m. p. 184.5—185° (decomp.); this on heating to 200° passes into the corresponding lactam (*benzoylenediethylpyrrolone*),

$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \\ \text{CO} \text{---} \text{N} \cdot \text{C}_2\text{H}_5 \end{array} > \text{CO},$$

colourless needles, m. p. 71°.

α -Phthalimino- α -methyl-*n*-butyryl chloride in a similar manner with ethyl sodiomalonate gives the corresponding *phthaliminomethylbutyric anhydride*, cubes, m. p. 183°, insoluble in water, together with the expected sodium derivative, from which carbon dioxide liberates *ethyl γ -phthalimino- β -keto- γ -methyl-*n*-pentanedicarboxylate*,



this is a neutral oil which gives an intense coloration with ferric chloride. When this substance is heated in alcoholic solution with sodium ethoxide, or its sodium derivative heated in alcohol, a soluble sodium salt is produced, from which hydrochloric acid frees an isomeric

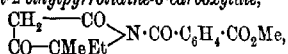
pyrrolidine derivative,
$$\begin{array}{c} \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CO} \\ \text{CO} \text{---} \text{CMeEt} \end{array} > \text{N} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}, \text{ m. p. 110}^\circ,$$

which on heating with dilute acid is converted into *carbethoxybenzoyl-methylethyletetracaric acid* [*ethyl 3:5-diketo-1-benzoyl-2-methyl-2-ethylpyrrolidine-*o*-carboxylate*],

$$\begin{array}{c} \text{CH}_2 \text{---} \text{CO} \\ \text{CO} \text{---} \text{CMeEt} \end{array} > \text{N} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et},$$
 an acidic substance, m. p. 186—187°. The application of sodium methoxide to the same oily ethyl ester, or of methyl alcohol to its sodium derivative in a similar manner, causes a replacement of ethyl by methyl, the

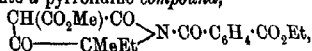
pyrrolidine derivative, prisms, m. p. 139—140°, produced being of the structure
$$\begin{array}{c} \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CO} \\ \text{CO} \text{---} \text{CMeEt} \end{array} > \text{N} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me};$$
 the acidity of this

substance is sufficient to cause its aqueous solution when heated to eliminate the carbethoxy-group with formation of *methyl 3:5-diketo-1-benzoyl-2-methyl-2-ethylpyrrolidine-*o*-carboxylate*,



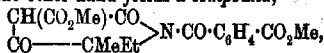
m. p. 209°, which reacts with bromine in chloroform solution, giving a neutral *tribromo-derivative*, m. p. 166—167°, by displacement of the methylene hydrogen atoms in the ring.

α -Phthalimino- α -methyl-*n*-butyryl chloride reacts with methyl sodiomalonate, yielding needles or prisms of *methyl γ -phthalimino- β -keto- γ -methyl-*n*-pentanedicarboxylate*, m. p. 98—99°, which colours ferric chloride blood-red. This substance with sodium ethoxide undergoes rearrangement into a *pyrrolidine compound*,



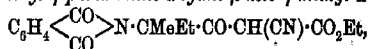
needles, m. p. 108—109° (of which an isomeride, m. p. 139—140°, has been described above), which when boiled with water yields the

pyrrolidine derivative, m. p. 186—187°, described earlier. Sodium methoxide on the other hand yields a compound,



prisms, m. p. 146—147°, which is more acid in character than acetic acid, and which easily loses the carbomethoxy-group, producing the pyrrolidine derivative, m. p. 209°.

The action of ethyl sodioacetoacetate on α -phthalimino- α -methyl-*n*-butyryl chloride gives a yellow sodium derivative, from which acetic acid liberates ethyl γ -phthalimino- α -cyano- β -keto- γ -methyl-*n*-hexoate,



m. p. 140°; this loses carbon dioxide when boiled with water, but the decomposition is not a simple one.

The pyrrolone condensation observed with phthaliminoethyl-*n*-butyryl chloride and excess of ethyl or methyl sodiomalonate occurs under the same conditions with the phthaliminomethylbutyryl compounds. Methyl

benzoylenemethylethylpyrrolonecarboxylate, $\text{C}_6\text{H}_4\cdot\text{C}=\text{C}(\text{CO}_2\text{Me})\cdot\text{CO}\cdot\text{N}\cdot\text{CMeEt}\cdot\text{CO}$,

forms yellow prisms, m. p. 130—131°; the corresponding yellow ethyl ester forms prisms, m. p. 112°. Both these esters react with hydrobromic acid, D 1.48, producing methylethylpyrrolonebenzoic acid hydrobromide, yellow needles, from which alkali in theoretical

quantity separates the free acid, $\text{C}_6\text{H}_4\cdot\text{C}=\text{CH}\cdot\text{CO}\cdot\text{N}\cdot\text{CMeEt}\cdot\text{NH}_2$, prisms,

m. p. 177° (decomp.), which above its m. p. passes into benzoylenemethylethylpyrrolone, $\text{C}_6\text{H}_4\cdot\text{C}=\text{CH}\cdot\text{CO}\cdot\text{N}\cdot\text{CMeEt}$, needles, m. p. 94—95°.

If methyl γ -phthalimino- β -keto- γ -methyl-*n*-pentanedicarboxylate is submitted to the action of methyl iodide in boiling acetone solution it is methylated to methyl δ -phthalimino- γ -ketomethyl-*n*-hexane- β -

dicarboxylate, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{---} \text{N}\cdot\text{CMeEt}\cdot\text{CO}\cdot\text{CMe}(\text{CO}_2\text{Me})_2$, prisms, m. p.

104°; this substance, which gives no ferric chloride reaction, is converted by boiling hydrochloric acid into oily γ -amino- γ -methylhexan- δ -one,



hydrochloride, crystalline; picrate, leaflets, m. p. 147—148°. D. F. T.

3-Nitropyridine and some of its Reduction Products. FRANK FRIEDL (*Monatsh.*, 1913, 34, 759—767).—The nitration of pyridine (A., 1912, i, 299) is most conveniently effected by the gradual addition of a solution of potassium nitrate in nitric acid (D 1.5) to a mixture of pyridine with an excess of sulphuric acid at 290—300°. It has already been shown that the product, 3-nitropyridine, is convertible by energetic reduction in acid solution into 3-aminopyridine, but it is now found that the analogy to nitrobenzene is still greater, extending to the successive formation of an azoxy-, azo-, and hydrazo-derivative when reduced in alkaline media.

3-Nitropyridine forms colourless needles, m. p. 41°, b. p. 216°;

hydrochloride, colourless leaflets, m. p. 154°; *sulphate*, hygroscopic crystals; *aurichloride*, yellow needles, m. p. 140°; *platinichloride*, broad, yellow needles, decomp. at 254°; *argenlonitrate*,

$(C_5H_4O.N)_2, AgNO_3$,
colourless needles, m. p. 175—176°.

When 3-nitropyridine is treated with a boiling solution of arsenious oxide in aqueous sodium hydroxide under reflux, it is reduced almost quantitatively to the corresponding *azopyridine*, silky needles, m. p. 130—131°, to a yellow liquid, which can be further reduced by zinc dust and alcoholic sodium hydroxide to *azopyridine*, orange-red needles, m. p. 142°, the yield again being almost the theoretical. The application of sodium methoxide as reducing agent for the production of the azoxy-compound and of iron filings for the azo-compound is unsatisfactory, yielding a complex mixture in each case and consequently an impure product.

If azopyridine is treated with zinc dust and boiling aqueous alcoholic sodium hydroxide in an atmosphere of hydrogen, reduction occurs with the formation of an 80% yield of *hydrazopyridine*, colourless needles, m. p. 202°; the pure substance is stable, but in alkaline alcoholic solution it undergoes atmospheric oxidation, especially readily on warming, with the production of azopyridine. It was not found possible to reduce hydrazobenzene further.

Partial nitration of pyridine occurs when nitric acid vapour is led into boiling pyridine nitrate, but there are formed simultaneously with 3-nitropyridine, also three other basic substances, m. p. 80°, 120, and 258° respectively; oxides of nitrogen in place of nitric acid lead to a similar result. Pyridine sulphate likewise gives a little 3-nitropyridine, but the main portion of the product consists of an oily mixture, b. p. 240—300°, of basic nature, from which could be isolated a base, woolly needles, m. p. 110°; *nitrate*, m. p. 245°; the base is very resistant to oxidising and reducing agents, and it is possibly related to the polymerised nitropyridine obtained by Spencer (P., 1903, 19, 79).

D. F. T.

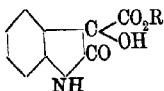
Syntheses of the Indole Group. IV. Basic Properties of Indoles, and Polymerides of Indoles. BERNARDO ODDO (*Gazzetta*, 1913, 43, i, 385—394. Compare A., 1912, i, 649).—The publication of the author's results on polymeric indoles has been anticipated to some extent by that of Keller (this vol., i, 403). Di-indole hydrochloride (compare Keller, *loc. cit.*) is a microcrystalline powder, m. p. 180°, forming a yellow liquid. It can be prepared by the prolonged action of dilute aqueous hydrochloric acid on indole at the ordinary temperature, or by treating indole with concentrated hydrochloric acid for a few minutes, as well as by the action of hydrogen chloride on an anhydrous ethereal solution of indole.

α-Methylindole hydrochloride, $C_8H_9N.HCl$, may be obtained by the action of hydrogen chloride on an anhydrous ethereal solution of *α-methylindole*.

The author gives also the results of some preliminary experiments regarding the power of indoles to form simple or double salts.

R. V. S.

Condensation of Primary and Secondary Aromatic Amines with Mesoxalic Esters. Synthesis in the Indole Series. ALFRED GUYOT and J. MARTINET (*Compt. rend.*, 1913, 156, 1625—1628).—Schmitt (A., 1905, i, 585) and Curtiss, Hill and Lewis (A., 1911, i, 366) obtained anilino-derivatives of the type $\text{NHPh}\cdot\text{C}(\text{CO}_2\text{R})_2\cdot\text{OH}$; $\text{NPh}\cdot\text{C}(\text{CO}_2\text{R})_2$; $\text{NHPh}\cdot\text{C}(\text{CO}_2\text{R})_2\cdot\text{NHPh}$ by the interaction of aromatic amines with mesoxalic esters. The authors have, however,



obtained, as principal product of such reactions an ester of dioxindole-3-carboxylic acid (annexed formula), which is saponified by aqueous potassium hydroxide in the absence of air, giving the corresponding dioxindole, carbon dioxide being eliminated. In an open vessel oxygen is rapidly absorbed, and the product formed is the corresponding isatin. The amine is warmed with the mesoxalic ester in acetic acid solution at 60° for one hour, and then the acid and residual amine are removed by steam. From the product any phenyltartronic acid produced is extracted with hydrochloric acid, and the residual indole derivative is crystallised from ether.

From *p*-toluidine the authors have prepared *methyl 5-methyldioxindole-3-carboxylate*, m. p. 251° , the *ethyl ester*, m. p. 212° , *5-methyldioxindole*, m. p. 210° , and the corresponding isatin.

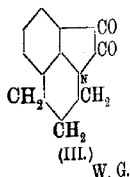
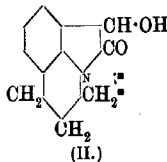
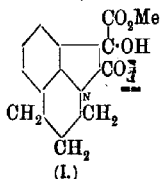
From β -naphthylamine, *methyl 3-hydroxy-2-ketodihydro- $\beta\beta$ -naphthindole-3-carboxylate*, m. p. above 300° , the *ethyl ester*, m. p. 210° , and the corresponding dioxindole and isatin.

From methylaniline, *methyl 1-methyldioxindole-3-carboxylate*, m. p. 217° , the *ethyl ester*, m. p. 130° , *methyl p-methylaminophenyltartronate*, m. p. 85° , and the dioxindole and isatin.

From ethylaniline, *ethyl 1-ethyldioxindole-3-carboxylate*, m. p. 141° , *ethyl p-ethylaminophenyltartronate*, m. p. 65° , the dioxindole, and isatin.

From ethyl- β -naphthylamine, *ethyl 2-hydroxy-3-keto-1-ethyldihydro- $\beta\beta$ -naphthindole-3-carboxylate*, m. p. 181° , the *dioxindole*, m. p. 172° , and the *isatin*, fine red needles, m. p. 173° .

From tetrahydroquinoline, *methyl 1:7-trimethylenedioxindole-3-carboxylate* (formula I), m. p. 188° , the *ethyl ester*, m. p. 174° , *1:7-trimethylenedioxindole* (formula II), m. p. 160° , and *1:7-trimethylenesisatin* (formula III), deep red prisms, m. p. 195° .



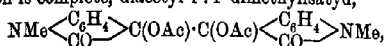
W. G.

1-Methylisatins. MORITZ KOHN and ALFONS OSTERETZER (*Monatsh.*, 1913, 34, 787—794).—In the preparation of 1-methylisatin from isatin there is no necessity to isolate the intermediate

sodium derivative of isatin (compare Heller, A., 1907, i, 442), and the subsequent reaction with methyl iodide in a sealed tube can also be avoided. If isatin is treated with the calculated quantity of 25% methyl-alcoholic potassium hydroxide, the separation of the blue potassium derivative gives rise to a paste which on the addition of methyl sulphate (under reflux) enters into reaction so vigorously that the mixture boils; 1-methylisatin can be easily separated from the reaction mixture (compare Friedländer and Kielbasinski, A., 1911, i, 1031).

Following a similar course 5-bromoisatin can be converted into 5-bromo-1-methylisatin, red, microscopic needles, m. p. indistinct at 164°, and 5:7-dibromoisatin into 5:7-dibromo-1-methylisatin, red, microscopic needles, m. p. indistinct at 171°. In these cases the sodium compounds react less vigorously with methyl sulphate than does the sodium compound of the unsubstituted isatin.

If carefully dried methylisatin is treated in boiling acetic anhydride containing a little acetic acid, with small quantities of zinc dust until decolorisation is complete, diacetyl-1:1'-dimethylisatyl,



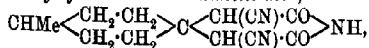
colourless, rhombohedral crystals, m. p. 218–220°, is obtained.

1-Methylisatin reacts with magnesium phenyl bromide in ethereal solution, giving a yellow, microcrystalline substance, $\text{C}_{21}\text{H}_{17}\text{ON}$, m. p. 145°; this is probably of the structure $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{CPh} \\ | \\ \text{NMe} - \text{CPh} \end{array} \text{O}$, produced by elimination of the elements of water from the ditertiary alcohol first formed by the action of the Grignard reagent on the two ketonic groups.

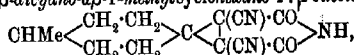
D. F. T.

Some Derivatives of *cyclo*Hexanone and the Three Methyl-*cyclo*hexanones. VINCENZO SQUINTANI (*Atti R. Accad. Sci. Torino*, 1912–13, 48, 675–686. Compare Guareschi, A., 1911, i, 792).—On warming a mixture of *cyclo*hexanone, ethyl cyanoacetate, and an alcoholic solution of methylamine, *aa'*-*dicyanocyclohexane*-1:1'-*diaceto*-*methylimide*, $\text{CH}_2 \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \right\rangle \text{C} \left\langle \begin{array}{c} \text{CH(CN)} \cdot \text{CO} \\ \text{CH(CN)} \cdot \text{CO} \end{array} \right\rangle \text{NMe}$, is produced; it has m. p. 175°. Its aqueous solution, when neutralised by ammonia, gives a blue precipitate with copper sulphate and a white, flocculent precipitate with silver nitrate. When treated with bromine it yields a white, flocculent compound, probably the *di*bromide, and when this is boiled with 10% alcoholic formic acid, *aa'*-*dicyano*-*aβ*-*cyclohexane*-*succinomethylimide*, $\text{CH}_2 \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \right\rangle \text{C} \left\langle \begin{array}{c} \text{C(CN)} \cdot \text{CO} \\ \text{C(CN)} \cdot \text{CO} \end{array} \right\rangle \text{NMe}$, is formed; it is a white, crystalline substance, m. p. 222°.

When a mixture of 1-methyl*cyclo*hexan-4-one, ethyl cyanoacetate and alcoholic ammonia is kept for some hours, an ammoniacal salt is deposited; from this, by the action of dilute acid, the *imide* of *aa'*-*dicyano*-1-methyl*cyclo*hexan-4:4'-*diacetic acid*,

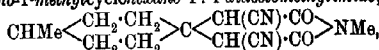


m. p. 210—211°, is obtained. Its *copper* salt is a chestnut-coloured precipitate which becomes yellowish-green; when it is made anhydrous and heated, it assumes at about 120° a red tint, which disappears on cooling. The imide of m. p. 210—211° yields a *dibromo*-derivative, from which *αβ*-dicyano-*αβ*-1-methylcyclohexane-4 : 4-succinimide,

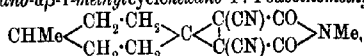


m. p. 207—208°, can be prepared.

αα'-Dicyano-1-methylcyclohexane-4 : 4-diacetomethylimide,



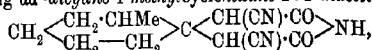
has m. p. 181—182°. It yields a crystalline *bromo*-derivative, m. p. 137°, which on treatment with an aqueous solution of sulphurous acid gives *αβ*-dicyano-*αβ*-1-methylcyclohexane-4 : 4-succinimethylimide,



m. p. 182—183°.

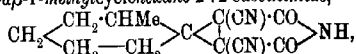
1-Methylcyclohexan-2-one yields similar products.

The *ammonium* salt, $\text{C}_{13}\text{H}_{18}\text{O}_2\text{N}_4$, obtained from 1-methylcyclohexan-2-one, ethyl cyanoacetate, and alcoholic ammonia has m. p. 165°. The corresponding *αα'*-dicyano-1-methylcyclohexane-2 : 2-diacetimide,



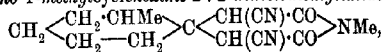
has m. p. 210°. Its *copper* salt is a rusty-red precipitate which turns bluish-green.

αβ-Dicyano-*αβ*-1-methylcyclohexane-2 : 2-succinimide,



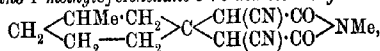
is a microcrystalline substance, m. p. 235—236°.

αα'-Dicyano-1-methylcyclohexane-2 : 2-diacetomethylimide,



has m. p. 181—182°.

αα'-Dicyano-1-methylcyclohexane-3 : 3-diacetomethylimide,



has m. p. 154°; in its preparation, a substance of m. p. 195—198° is also met with. R. V. S.

Preparation of Nitro-*N*-alkylcarbazoles. FARRBERKE, TOHN, MEISTER, LUCIUS & BRÜNING (D.R.-P. 259504).—The nitration of *N*-alkylcarbazoles has previously given rise to a mixture of difficultly separable nitro-derivatives, but it is now found that if nitrous acid is employed definite compounds are obtained.

Nitro-9-ethylcarbazole, yellow crystals, m. p. 128°, is obtained when 9-ethylcarbazole (200 parts) in benzene (1000 parts) is mixed with a concentrated aqueous solution of sodium nitrite, and 600 parts of hydrochloric acid slowly added with efficient stirring at the ordinary temperature and the mixture subsequently boiled. *Nitro-9-methylcarbazole* forms small needles, m. p. 147—148°. F. M. G. M.

Preparation of Arylanthraquinone Derivatives. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 259037. Compare this vol., i, 95—105).—4-*p*-Toluidino-1:2-anthrathiazole, dark blue needles, is obtained by boiling 1-amino-4-*p*-toluidinoanthraquinone-2-mercaptan with benzaldehyde (3 parts) and nitrobenzene (3 parts); on sulphonation it furnishes a compound which dyes wool a fast violet colour.

The analogous compound from 2-amino-1-*p*-toluidino-3-thioanthraquinone and benzaldehyde is obtained in brownish-violet prisms.

F. M. G. M.

Syntheses of Alkyloxymalachite-greens by means of Magnesium Aryl Haloids. EMIL VOTOČEK and J. MATĚJKA (*Ber.*, 1913, 46, 1755—1759).—The present work has been undertaken with the object of gaining insight into certain discrepancies observed in condensations with tetramethyldiaminobenzhydrol (Votoček and Jelinek, A., 1907, i, 245; Votoček and Krauz, A., 1909, i, 518). The use of Grignard's reagents presents the advantage that operations can be performed at a comparatively low temperature. A series of alkyloxymalachite-greens has been prepared from the magnesium derivatives of halogenated phenol ethers and Michler's ketone on the one hand, and from methyl anisate and the magnesium derivative of *p*-bromodimethylaniline on the other.

p-Methoxymalachite-green, obtained by the action of magnesium *p*-anisyl bromide on an ethereal suspension of Michler's ketone and subsequent decomposition of the product formed with hydrochloric acid and reduction with sodium hyposulphite, has m. p. 106°, and is identical with the compound prepared from anisaldehyde and dimethylaniline. The same substance is formed when ethereal solutions of magnesium *p*-dimethylaminophenyl bromide and methyl anisate (m. p. 46°, b. p. 255°) are mixed.

p-Ethoxymalachite-green is obtained in a similar manner from magnesium *p*-phenetole bromide and Michler's ketone, and is identical with the substance produced from *p*-ethoxybenzaldehyde and dimethylaniline.

m-Methoxymalachite-green is prepared by the gradual addition of an ethereal solution of magnesium *m*-methoxyphenyl iodide to a boiling solution of Michler's ketone in benzene and subsequent reduction to the leuco-base. It has m. p. 123°, and is identical with *m*-methoxytetramethyldiaminotriphenylmethane prepared from *m*-methoxybenzaldehyde and dimethylaniline.

o-Methoxymalachite-green, prepared from magnesium *o*-methoxyphenyl iodide and Michler's ketone, is identical with the product obtained from *o*-methoxybenzaldehyde and dimethylaniline. H. W.

Further Investigations of Alkyloxy-derivatives of Malachite-Green. EMIL VOTOČEK and J. KÖHLER (*Ber.*, 1913, 46, 1760—1769. Compare A., 1907, i, 245; 1909, i, 518; also previous abstract).—A difference has been previously noted between the leuco-bases obtained from alkyloxybenzaldehydes and dimethylaniline, and those prepared

from tetramethyl-*p*-diaminobenzhydrol and phenolic ethers. This is now attributed to the transformation of the methoxy- into the hydroxy-group under the conditions of the experiments. The work has been further extended to ethoxy-derivatives and to polyhydroxy-phenols.

Tetraethyldiaminobenzhydrol is prepared by reduction of tetraethyldiaminobenzophenone by sodium and alcohol or by oxidation of tetraethyldiaminodiphenylmethane, m. p. 41° , with lead peroxide. It condenses with phenol in the presence of hydrochloric acid, forming *p*'-hydroxy-*p*'' : *p*'''-tetraethyldiaminotriphenylmethane, m. p. $110-111^{\circ}$, which is also obtained by heating *p*-hydroxybenzaldehyde and diethylaniline with hydrochloric acid and a little alcohol at 125° for twelve hours. When oxidised with chloranil, it gives a green dye which becomes violet on addition of alkali.

Tetraethyldiaminobenzhydrol does not react readily with anisole in the presence of hydrochloric acid, and does not yield a uniform product. On the other hand, anisaldehyde readily condenses with diethylaniline, yielding *p*'-methoxy-*p*'' : *p*'''-tetraethyldiaminotriphenylmethane, m. p. 65° . In the hope of obtaining an abnormal base of betaine-like structure (A., 1909, i, 519), the substance was heated with hydrochloric acid at 120° during two hours. The products of the action consisted of methyl chloride and *p*'-hydroxy-*p*'' : *p*'''-tetraethyldiaminotriphenylmethane. Since hydrochloric acid was found to have a similar action in the methoxy-series, the supposed existence of a larger number of isomerides is disproved, and the supposition of a betaine-like structure is rendered unnecessary.

p'-Hydroxy-*p*'' : *p*'''-tetramethyldiaminotriphenylmethane, m. p. 165° , is obtained from *p*-hydroxybenzaldehyde and dimethylaniline, and also from phenol and Michler's hydrol. The same substance is isolated with difficulty from the product of the action of hot concentrated hydrochloric acid on a mixture of anisole and Michler's hydrol, the methyl group being partly eliminated during the reaction. That this is actually the case is proved by the isolation of the acetyl derivative of *p*'-hydroxy-*p*'' : *p*'''-tetramethyldiaminotriphenylmethane, m. p. $145-146^{\circ}$, by the action of acetic anhydride on the above product, whereas, under the conditions employed, this reagent does not attack *p*'-methoxy-*p*'' : *p*'''-tetramethyldiaminotriphenylmethane. The latter substance evolves methyl chloride when heated with hydrochloric acid at 120° , and is converted into *p*'-hydroxy-*p*'' : *p*'''-tetramethyldiaminotriphenylmethane. When the last-named substance is acted on by methyl sulphate, an impure product is obtained from which the hydroxy-compound can be regained after repeated crystallisation (compare A., 1909, i, 519).

Similarly, the compound obtained from Michler's hydrol and phenetole, and that from *p*-ethoxy-leucomalachite-green and hydrochloric acid are shown to be *p*-hydroxy-leucomalachite-green.

The methyl group is also completely eliminated from *m*-methoxy-leucomalachite-green by treatment with hydrochloric acid at 120° during two hours. *o*-Methoxy-leucomalachite-green is not completely decomposed under these conditions.

p-Dimethoxyleucomalachite-green, m. p. 129—130°, is obtained by the addition of an ethereal solution of magnesium *p*-dimethoxyphenyl bromide to a solution of Michler's ketone in ether and benzene, and subsequent reduction of the dye formed by means of sodium hyposulphite, whilst the same substance can also be prepared by the condensation of Michler's hydrol and quinol dimethyl ether in the presence of hydrochloric acid and alcohol. When oxidised by chloranil, it yields a green dye, stable towards alkalis.

Michler's ketone may be condensed with catechol in the presence of phosphoryl chloride, and the dye produced is readily reduced to dihydroxytetramethyldiaminotriphenylmethane, m. p. 162—163°. The substance is identical with that obtained from protocatechualdehyde and dimethylaniline, or from catechol and Michler's hydrol. Under similar conditions, resorcinol yields a green dye, which becomes violet on addition of alkali; the corresponding leuco-base has not been obtained in the crystalline state. Quinol does not condense with Michler's ketone under these conditions.

The behaviour of these leuco-bases as photographic developers has been investigated. Reducing power is only observed in those cases in which the hydroxyl groups are in the ortho- or para-position.

H. W.

Influence of the Halogens on Phototropy in Hydrazones.
II. FERDINANDO GRAZIANI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 623—629. Compare A., 1910, i, 777).—The paper describes the hydrazones derived from the three isomeric chlorophenylhydrazines.

None of the *o*-compounds is phototropic, all the *m*-derivatives are phototropic, whilst four of the eight *p*-derivatives prepared are phototropic.

Benzaldehyde-o-chlorophenylhydrazone, $C_6H_4Cl \cdot NH \cdot N : CHPh$, crystallises in minute, colourless needles, m. p. 73°.

Anisaldehyde-o-chlorophenylhydrazone, $C_6H_4Cl \cdot NH \cdot N : CH \cdot C_6H_4 \cdot OMe$, is a white, crystalline powder, m. p. 67°.

Cuminaldehyde-o-chlorophenylhydrazone,
 $C_6H_4Cl \cdot NH \cdot N : CH \cdot C_6H_4 \cdot CHMe_2$,
forms slightly yellow needles, m. p. 67°.

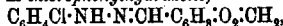
Cinnamaldehyde-o-chlorophenylhydrazone,
 $C_6H_4Cl \cdot NH \cdot N : CH \cdot CH : CHPh$,
crystallises in flat, sulphur-yellow needles, m. p. 99°.

Piperonaldehyde-o-chlorophenylhydrazone,
 $C_6H_4Cl \cdot NH \cdot N : CH \cdot C_6H_4 \cdot O_2 \cdot CH_2$,
forms slightly yellow, flat needles, m. p. 96°.

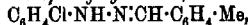
Anisaldehyde-m-chlorophenylhydrazone,
 $C_6H_4Cl \cdot NH \cdot N : CH \cdot C_6H_4 \cdot OMe$,
crystallises in flat, colourless needles, m. p. 135°.

Cuminaldehyde-m-chlorophenylhydrazone,
 $C_6H_4Cl \cdot NH \cdot N : CH \cdot C_6H_4 \cdot CHMe_2$,
forms flat, colourless needles, m. p. 131°, and is very phototropic.

Cinnamaldehyde-m-chlorophenylhydrazone,
 $C_6H_4Cl \cdot NH \cdot N : CH \cdot CH : CHPh$,
is a yellow, crystalline powder, m. p. 120°.

Piperonaldehyde-m-chlorophenylhydrazone,

forms minute, colourless needles, m. p. 95° ; it is very strongly phototropic.

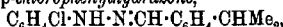
*Salicylaldehyde-m-chlorophenylhydrazone is very feebly phototropic.**p-Tolualdehyde-m-chlorophenylhydrazone,*

is a white, crystalline powder, m. p. 112° . ●

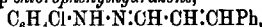
Benzaldehyde-*p*-chlorophenylhydrazone has been prepared by Hewitt (T., 1893, 63, 873), who gave m. p. 127° ; the present author finds m. p. 132° . The substance is phototropic.

Anisaldehyde-p-chlorophenylhydrazone, C₆H₄Cl·NH·N·CH·C₆H₄·OMe,

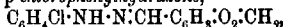
forms colourless leaflets, m. p. 150° , and is not phototropic.

Cuminaldehyde-p-chlorophenylhydrazone,

forms slightly yellow needles, m. p. 131° , and is very phototropic.

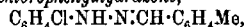
Cinnamaldehyde-p-chlorophenylhydrazone,

crystallises in yellowish-green needles, m. p. 136° ; it is phototropic.

Piperonaldehyde-p-chlorophenylhydrazone,

forms slightly yellow leaflets, m. p. 143° , and is not phototropic.

Salicylaldehyde-*p*-chlorophenylhydrazone has m. p. 173° (Auwers, A., 1909, i, 440, gave 169 — 170°). It is not phototropic.

p-Tolualdehyde-p-chlorophenylhydrazone,

crystallises in slightly yellow needles, and is feebly phototropic.

Vanillin-p-chlorophenylhydrazone,

forms flat, slightly yellow needles, m. p. 135° . It is not phototropic.

R. V. S.

The Formation of Dipiperidyls in the Electrolytic Reduction of Pyridine. BRUNO EMMERT (*Ber.*, 1913, 46, 1716—1719).—From the formation of azobenzene and pinacone respectively in the reduction of nitrobenzene and acetone, and of phenylmethylpyrrolidone (Emmert, A., 1907, i, 339) in the reduction of a mixture of nitrobenzene and lævulic acid, it would appear that the first stage of the reduction is the production of free radicles which subsequently couple together. The electrolytic reduction of pyridine (Ahrens, A., 1897, i, 368), which has been believed to yield only piperidine, might therefore be expected to give rise to at least a small quantity of some binuclear product.

The reduction of pyridine at lead cathodes with a current density of 17.1 amps. per sq. dm. in diluted sulphuric acid is found to give actually much piperidine accompanied by less volatile products including 4:4'-dipiperidyl, m. p. 158 — 160° , 2:2'-dipiperidyl, b. p. 258 — 260° (corr.), and a high boiling resinous substance the molecule of which probably includes a higher number of piperidine nuclei; these less volatile products amounted to more than 10% of the pyridine taken.

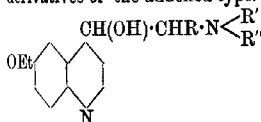
D. F. T.

[Preparation of a Condensation Product from 5:7-Dichloroisatin and 6-Chloroindoxyl.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 258258).—When a hot acetic acid solution of 5:7-dichloroisatin (220 parts) is treated with a similar solution of 6-chloroindoxyl (167 parts), some concentrated sulphuric acid added and the mixture warmed, it furnishes a compound crystallising in glistening, brown metallic needles. Differently substituted indoxyls and isatins can be employed for this reaction. F. M. G. M.

Preparation of New Condensation Products from Indigotin and its Halogen Derivatives. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 259145).—When indigotin derivatives are treated with aromatic acid haloids in the presence of a condensing agent, they furnish compounds which dye wool in yellow shades.

The compound obtained by the action of benzoyl chloride on indigotin in the presence of copper powder forms yellowish-green needles, m. p. 275—276°. F. M. G. M.

Synthetic Bases Closely Related to the Cinchona Alkaloids. ADOLF KAUFMANN (*Ber.*, 1913, 46, 1823—1837).—The difference in toxicity between quinine and quinotoxine is not due to the rearrangement of the nitrogen in the quinuclidine ring into a secondary amino-group with a free hydrogen atom, for methylcinchotoxine is just as active as cinchotoxine. Experiments by A. Warschawski have now shown that 4-quinolyl ketone (A., 1912, i, 1017), although it is chemically related to quinotoxine, is antipyretic, and only very slightly poisonous, from which it appears that the ketone group is not responsible for the toxicity. On the other hand, the ethyl ester of meroquinine and especially the reduction product, ethyl cincholeuponate, are very powerful poisons. However, the author maintains his former hypothesis (*ibid.*) that the specific action of quinine is connected with the presence of an adrenaline-like grouping, and has now prepared derivatives of the annexed type.

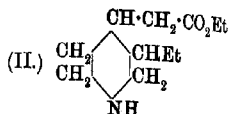
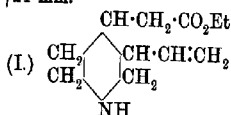


It was found that 6-alkoxy-4-quinolyl ketones with methyl or methylene attached to the carbonyl group react with halogens, giving derivatives which condense with primary amines, and that the new substances could be reduced to hydroxy-compounds of the above type. They all have the same physiological effect as quinine, and give the same fluorescence and respond to the thalleoquinine test. The process is easily carried through, and it thus becomes possible to prepare numerous analogues of quinine.

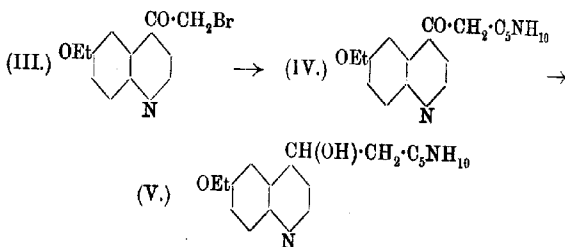
I. [With MAX HUBER and A. STETTACHER].—The cinchotoxine obtained by boiling 10 grams of cinchonine hydrochloride with 400 c.c. of 0.001% hydrochloric acid for fifty hours was extremely small in amount (compare Biddle, A., 1912, i, 296), but was characterised as the *phenylhydrazone-picrate*, which separated in microscopic, red needles, m. p. 200°, when phenylhydrazine and picric acid were added

to the alkaline, ethereal extract. The reaction is sensitive in a dilution of 1 in 2500.

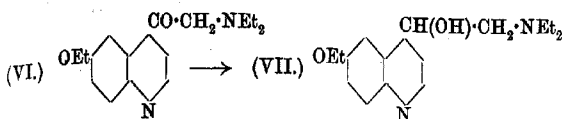
II. [With OTTO ZELLER and MAX HUBER].—Meroquinine was prepared by the hydrolysis of quinine with 25% phosphoric acid at 180° (Koenigs, A., 1894, i, 392). The *p*-methoxyepidine phosphate separated on cooling in large, grey, lanceolate crystals, m. p. $208-210^{\circ}$, and the filtrate was fractionally precipitated with phosphotungstic acid. The meroquinine obtained from the precipitate by means of baryta was esterified, and the hydrochloride of the ethyl ester (I) (Koenigs, A., 1906, i, 762), reduced by hydrogen and colloidal palladium to the hydrochloride of ethyl cincholeuponate, which formed beautiful white needles, m. p. 158° , $[\alpha]_D^{25} + 5.71^{\circ}$ (compare Skraup, A., 1895, i, 484). The free ester (II) is a colourless liquid, b. p. $140^{\circ}/14$ mm., $[\alpha]_D^{25} - 17.2^{\circ}$, which reacts violently with methyl iodide, giving ethyl *N*-methylcincholeuponate, $C_{12}H_{25}O_2N$, as a colourless oil, b. p. $139^{\circ}/21$ mm.



III. [With AUGUST POLL and HEINRICH PEYER].—6-Ethoxy-4-quinolyl methyl ketone (this vol., i, 294) was warmed with bromine in hydrobromic acid, when the hydrobromide of 6-ethoxy-4-quinolyl bromomethyl ketone separated in lemon-yellow crystals, m. p. 207° . The hydrochloride, m. p. 190° , crystallised when hydrochloric acid was used. The free base (III) forms yellow needles, m. p. $104-105^{\circ}$, but is not so stable as the salts. When the hydrobromide is added to piperidine, diethylamine or dimethylamine in benzene or ether, the salt of the primary base is precipitated, and the new amino-ketone is obtained by evaporating the filtrate or by precipitation in the form of a salt.



6-Ethoxy-4-quinolyl piperidinomethyl ketone (IV) crystallises in light yellow, sparkling leaflets, m. p. 158° , and the hydrobromide forms long, white needles, m. p. $189-190^{\circ}$. 6-Ethoxy-4-quinolyl diethylamino-methyl ketone (VI) is a yellow, crystalline powder, m. p. 131° , which yields a neutral monobromide in white needles and a yellow dibromide, m. p. $193-194^{\circ}$, which reacts acidic. The dimethylamino-ketone, $C_{15}H_{19}O_2N_2$, forms yellow, prismatic columns, m. p. 132° .



The ketones are readily reduced by hydrogen in presence of palladium. 6-Ethoxy-4- β -piperidino- α -hydroxyethylquinoline (V) crystallises in white needles and plates, m. p. 85°, and the 6-ethoxy-4- β -diethylamino- α -hydroxyethylquinoline (VII) forms a very soluble hydrochloride in soft, white needles, m. p. 171°.

J. C. W.

Hydantoins. XXII. History of 2-Thiohydantoin. TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1913, 35, 780—784).—2-Thiohydantoin was first synthesised by Klason (*A.*, 1891, 179) by heating ethyl aminoacetate hydrochloride with potassium thiocyanate at 140—150°, but this work seems to have been overlooked by subsequent workers. Klason's observation has now been confirmed, but it has been found that the method gives too small a yield to be of practical value for preparing the compound. The reaction involves the intermediate formation of ethyl thiohydantoate. An attempt was therefore made to obtain 2-thiohydantoin by warming ethyl thiohydantoate with hydrochloric acid, but without success, hydrogen sulphide, ammonium chloride, and glycine hydrochloride being produced.

E. G.

Preparation of ω -Methyl Sulphites [and ω -Alkyl Sulphites] of Substituted Aminoarylpyrazolones. FARBERWERKE FORM. MEISTER, LUCIUS & BRÜNING (D. R.-P. 259503—259577).—An account of the preparation of compounds previously described (this vol., i, 401), by the action of formaldehyde and sodium hydrogen sulphite on substituted aminopyrazolones. The second patent states that the formaldehyde can be replaced by other aldehydes, and describes the compounds obtained from 4-amino-1-phenyl-2:3-dimethyl-5-pyrazolone with acetaldehyde, and with propaldehyde, both of which have m. p. 124—125°, the latter decomposing at 130°.

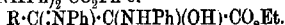
F. M. G. M.

Reactions of $\alpha\beta$ -Diketonic Esters. ANDRÉ WAHL and M. DOLL (*Bull. Soc. chim.*, 1913, [iv], 13, 468—485. Compare *A.*, 1905, 474; 1907, i, 217; 1911, i, 108; 1912, i, 536, 625; this vol., 473).—The interaction of these esters with various reagents is described, and a number of the compounds obtained have been characterised. Some of this work has been recorded already (*loc. cit.*). The following observations and compounds are new:

Action of α -diamines (*A.*, 1912, i, 536, 625).—Ethyl 2-methylquinazoline-3-carboxylate, m. p. 74°, forms colourless needles. Ethyl 2-methyl-1:4-naphthaquinazoline-3-carboxylate, m. p. 113—114°, forms slender, colourless needles. Ethyl 2-propyl-1:4-naphthaquinazoline-3-carboxylate, m. p. 83—84°, crystallises in long, colourless needles. Ethyl 2-n-butylquinazoline-3-carboxylate is an oil, but the corresponding acid, m. p. 86°, is crystalline. Ethyl 2-phenylquinazoline-3-carboxylate,

m. p. 62—63°, forms silky needles; the *propyl* ester, m. p. 72—73°, and the *isobutyl* ester, m. p. 71°, are both crystalline. *Ethyl 2-phenyl-1:4-naphthaquinazoline-3-carboxylate*, m. p. 116°, forms colourless needles.

Action of cyclic amines (A., 1912, i, 536, 625).—The aromatic esters condense with 2 mols. of the cyclic amines with the loss of $1\text{H}_2\text{O}$. The resulting compounds are probably best represented by the general formula $\text{R}\cdot\text{CO}\cdot\text{C}(\text{NPh})_2\cdot\text{CO}_2\text{Ph}$ or



Methyl benzoylglyoxalate yields a *dianilide*, m. p. 144—145°, crystallising in yellow needles from warm benzene, and a *di-p-toluidide*, m. p. 115—116°, forming lemon-yellow crystals. The *propyl* ester gives a *dianilide*, m. p. 88—89°, and the *isobutyl* ester a *dianilide*, m. p. 108—109°.

Action of hydroxylamine (A., 1907, i, 217; 1912, i, 536, 626).—With the exception of ethyl acetylglyoxalate, which yields a dioxime, all the esters yield monoximes when treated with hydroxylamine; thus methyl *p*-methoxybenzoylglyoxalate furnishes methyl oximinoanisoylacetate (this vol., i, 214, 532).

Action of phenylhydrazine (A., 1905, i, 474; 1912, i, 213, 536, 626; this vol., i, 532).—Ethyl *n*-valeroylglyoxalate yields 4-phenylhydrazino-1-phenyl-3-*n*-butyl-5-pyrazolone, m. p. 119—120°, crystallising in orange needles. Methyl anisoylglyoxalate in addition to the two compounds already described (A., 1912, i, 626) when boiled in acetic acid with 2 mols. phenylhydrazine yields 4-phenylhydrazino-1-phenyl-3-*p*-methoxyphenyl-5-pyrazolone (A., 1912, i, 213). Methyl benzoylglyoxalate may yield (1) the *additive product*, $\text{COPh}\cdot\text{C}(\text{OH})(\text{NH}\cdot\text{NHPh})\cdot\text{CO}_2\text{Me}$, m. p. 144—145°, or (2) a mixture of phenylhydrazinopyrazolone with the *monophenylhydrazone*, m. p. 76° (identical with methyl benzeneazobenzoylacetate) depending on the conditions of the reaction. *isoButyl benzoylglyoxalatephenylhydrazone*, m. p. 62—63°, forms hexagonal tablets. Unlike phenylhydrazine, *p*-nitrophenylhydrazine does not give rise to additive products, but yields either α -mono-*p*-nitrophenylhydrazones or *p*-nitrophenylhydrazinopyrazolones (*loc. cit.*).

Action of semicarbazide (A., 1907, i, 217; 1912, i, 536, 626).—The acyclic esters yield normal disemicarbazones, whilst the cyclic esters furnish compounds which have the composition of disemicarbazones with 1 mol. H_2O in addition. Probably 1 mol. of semicarbazide is added to the α -carbonyl, whilst the second condenses normally with the β -carbonyl group. Methyl benzoylglyoxalate yields a *compound*, m. p. 215°, of this type, which on recrystallisation is partly converted into a yellow *compound*, m. p. 292°, which may be a true disemicarbazone.

Action of hydrazine hydrate (A., 1912, i, 536, 626; this vol., i, 532).—Ethyl valeroylglyoxalate yields *diethyl-3:3'-rubazonic acid*, and ethyl hexoylglyoxalate gives *dihexyl-3:3'-rubazonic acid*. With cyclic esters additive products are formed consisting of 2 mols. of the ester and one of hydrazine hydrate when the reaction takes place in acetic acid. Such a product has been described for methyl anisoylglyoxalate, $\text{N}_2\text{H}_4[\text{C}(\text{OH})(\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{CO}_2\text{Me}]_2$ (A., 1912, i, 626); that yielded by methyl benzoylglyoxalate has m. p. 137°, and crystallises in yellow

spangles. In alcoholic solution the benzoylglyoxalates yield 3:3'-diphenylrubazonic acid (*loc. cit.*).

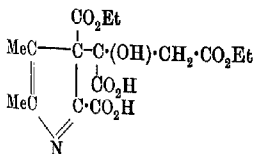
The benzoylglyoxalates condense with the benzoylacetates in presence of piperidine, forming compounds in which condensation has probably been effected by interaction of the β -ketonic ester with the α -carbonyl. The following *products* of this kind are described; they crystallise in colourless needles: methyl benzoylacetate with methyl benzoylglyoxalate, $\text{CO}_2\text{Me}\cdot\text{CBz}(\text{OH})\cdot\text{CHBz}\cdot\text{CO}_2\text{Me}$ (?), m. p. 120° ; ethyl benzoylacetate with methyl benzoylglyoxalate, m. p. $117-118^\circ$; methyl benzoylacetate with ethyl benzoylglyoxalate, m. p. $124-125^\circ$; methyl *o*-methoxybenzoylacetate with methyl benzoylglyoxalate, m. p. $136-137^\circ$ (compare A., 1907, i, 217).
T. A. H.

Behaviour of Diphenyltriketone with Amino-compounds. I. CARLO GASTALDI and F. CHERCHI (*Gazzetta*, 1913, 43, i, 299-303).—

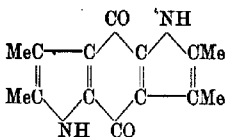
When alcoholic solutions of diphenyltriketone and *o*-phenylenediamine are mixed and cooled, benzoylphenylquinoxaline, $\begin{array}{c} \text{CPh} \text{---} \text{C} \text{---} \text{COPh} \\ | \qquad \qquad | \\ \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N} \end{array}$, separates in slightly yellow scales, m. p. 153° . Its constitution follows from the fact that it can also be obtained from bromodibenzoylcarbinyloacetate. When the solution from which the crystals of m. p. 153° separate is diluted with water, diphenyltriketone-*o*-phenylenediamine, $\text{COPh}\cdot\text{C}(\text{OH})_2\cdot\text{CPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, is obtained in colourless rosettes, m. p. 155° . When this compound is heated on the water-bath for ten hours in aqueous-alcoholic solution with hydrochloric acid, phenylbenziminazole hydrochloride, m. p. 343° , is produced. The phenylbenziminazole liberated from it has m. p. 294° (compare Japp and Meldrum, T., 1890, 57, 1043).
R. V. S.

Tetramethylpyrindoquinone and Some Other Derivatives of 2:3-Dimethylpyrrole. OSCAR PILOTY and K. WILKE (*Ber.*, 1913, 46, 1597-1603. Compare Piloty, A., 1910, i, 277).—The paper deals with the preparation of a quinone, tetramethylpyrindoquinone, from 2:3-dimethylpyrrole-4-carboxylic acid. The authors have also prepared 2:3-dimethyl-1-ethylpyrrole for comparison with their "hæmopyrrole-*e*," but have not yet been able to prepare "hæmopyrrole-*e*" picrate from it. They have found further that tri-substituted *C*-derivatives of pyrrole can yield bispyrrole picrates, so that the power to form bispyrrole derivatives and their picrates does not seem to follow any law.

The preparation of 4-ethyl hydrogen 2:3-dimethylpyrrole-4:5-dicarboxylate (A., 1912, i, 899) is simplified by using the tin double salt of β -aminobutan- γ -one, instead of that substance itself. The employment of ethyl hydrogen oxalacetate, instead of ethyl oxalacetate, presents no advantage, but it leads to the formation of a by-product, termed *aphaninester acid*, probably of the



annexed formula. This substance crystallises in hair-like needles, m. p. 156°. *Tetramethylpyrindoquinone* (annexed formula) is obtained by boiling 2:3-dimethylpyrrole-4-carboxylic acid (*loc. cit.*) with acetic anhydride for several hours; it crystallises in rhombic tablets, which are yellow by transmitted, red by reflected, light; at a high temperature the substance sublimes.



2:3-Dimethyl-1-ethylpyrrole-4-carboxylic acid, $C_9H_{13}O_2N$, is obtained by acting on 4-ethyl potassium 2:3-dimethylpyrrole-

4:5-dicarboxylate (*loc. cit.*) with ethyl sulphate in benzene solution, and saponifying the ester by means of boiling concentrated aqueous alkali; it forms thin rods, m. p. 156°. When compressed tablets of this acid are subjected to dry distillation, 2:3-dimethyl-1-ethylpyrrole, $C_8H_{11}N$, b. p. 59°/11 mm., is produced. If hydrogen chloride is passed into a dry ethereal solution of the substance, the bis-compound is obtained; it crystallises in a freezing mixture in long needles which melt at room-temperature.

Ethyl 1:2:3-trimethylpyrrole-4-carboxylate, $C_{10}H_{15}O_2N$ (prepared similarly, using methyl sulphate), forms flat, rhombic prisms, m. p. 52°. The acid, $C_8H_{11}O_2N$, forms stellar aggregates of small crystals, m. p. 229° (previously sintering and becoming slightly brown).

Ethyl 2:3-dimethylpyrrole-4:5-dicarboxylate, $C_{12}H_{17}O_4N$ (prepared by the action of ethyl sulphate on the potassium salt), forms rhombic leaflets, m. p. 110°. Its *picrate*, $C_{18}H_{20}O_{11}N_4$, crystallises in bright orange rods, m. p. 112—113°. The *picrate* of the methyl ethyl ester of the same acid (*loc. cit.*) forms straw-yellow needles, which sinter at 122°, and are completely melted at 140°; analysis gave the formula $C_{28}H_{35}O_{15}N_5$, indicating a bis-compound.

2:3-Dimethylpyrrole-4-carboxylic acid yields a *picrate*, $C_{20}H_{21}O_{11}N_5$, which forms compact, red rods, m. p. 143°.

R. V. S.

Existence of Phenyl-di-imide. STEFAN GOLDSCHMIDT (*Ber.*, 1913 46, 1529—1532. Compare Vaubel, A., 1900, i, 522; this vol., i, 519; Forster and Withers, T., 1913, 103, 266).—Vaubel's supposed phenyl-di-imide has been characterised by Forster and Withers as a mixture of aniline and phenylazoimide. The author has repeated Vaubel's experiments, and, employing conditions somewhat different from those used by Forster and Withers, finds that the product is pure phenylazoimide, b. p. 65—68°/12 mm., the identity of which is confirmed by the formation of a condensation product, m. p. 178—179°, with phenylacetonitrile (compare Dimroth, A., 1903, i, 129).

The author has further attempted to prepare di-imines by the oxidation of phenylhydrazine and *p*-bromophenylhydrazine. At the ordinary temperature, the action of oxidising agents, such as lead peroxide, silver oxide, or *p*-benzoquinone, etc., is accompanied by the evolution of nitrogen. Since the action of all these agents with the exception of *p*-benzoquinone ceases at 0°, the latter substance has alone been used.

When an ethereal solution of *p*-benzoquinone is gradually added to a

solution of *p*-bromophenylhydrazine in ether cooled to -60° with careful exclusion of moisture and carbon dioxide, a copious separation of quinoxaline occurs and a yellow filtrate is obtained from which nitrogen is evolved on warming. Addition of a solution of stannous chloride in ether causes regeneration of *p*-bromophenylhydrazine. Attempts to isolate the di-imine in the pure state were, however, unsuccessful. It appears to possess no tendency to form salts or double salts, and does not react with substances such as anhydrous hydrocyanic acid, diphenylketene, etc., at the low temperature necessitated by the instability of the substance. Tribromophenylhydrazine, which might be expected to yield a more stable oxidation product, is unaffected by *p*-benzoquinone.

H. W.

Iminoindigotin. ARTHUR BINZ and K. R. LANGE (*Ber.*, 1913, 46, 1691—1695).—When indigotin is shaken for two hours with alcoholic sodium ethoxide solution and the resultant additive product (compare Binz and Schädel, A., 1912, i, 317) shaken with a solution of zinc hydroxide in ammonia together with an excess of saturated alcoholic solution of ammonia, the resulting blue liquid after acidification with dilute hydrochloric acid deposits *iminoindigotin hydrochloride*; the sulphate is also sparingly soluble. The parent substance is evidently more reactive than indigotin, for the blue solution obtained before acidification can be completely oxidised by air to a brown substance, whilst hydrogen sulphide reduces the solution to a vat which on re-oxidation yields, not the imine, but a new substance which dissolves in alkali to a red, and in alcohol to a brown, solution. The iminoindigotin hydrochloride can be reduced by gentle warming with sodium hyposulphite, giving a greyish-white leuco-compound. The aqueous solution of the hydrochloride itself dyes wool and mordanted cotton, producing similar shades to indigotin.

If the blue solution obtained by the interaction of the additive compound of sodium ethoxide and indigotin with zinc hydroxide and ammonia is treated with much water instead of with acid, a zinc salt, $(C_{16}H_{10}ON_2)_2Zn$, a bluish-green, amorphous substance, soluble in chloroform and acetone, is obtained. This acid character of iminoindigotin is different from the power by which indigotin forms additive compounds because the colour is relatively unaffected.

The free *iminoindigotin*, $C_{16}H_{11}ON_3$ (compare Thiele and Pickard, A., 1898, i, 493), was obtained most satisfactorily by reducing the sulphate with aqueous sodium hydroxide and hyposulphite and re-oxidising the yellow solution; the deep blue product is obtained crystalline with difficulty, and decomposes without melting; it is probably not a pure substance, but possibly a mixture of isomerides, so that the formula $C_6H_4 \begin{smallmatrix} \diagup C(NH) \\ \diagdown NH \end{smallmatrix} \diagup C \begin{smallmatrix} \diagdown CO \\ \diagup NH \end{smallmatrix} \diagdown C_6H_4$ must be accepted with reserve. The formation of the substance however, seems to supply further evidence in favour of the view that one-half of the indigotin molecule is more reactive than the second (compare Claasz, A., 1912, i, 513).

The halogen-indigotins, also indigo-red and "thioindigo," likewise form imino-derivatives, whilst by applying methylamine in the original

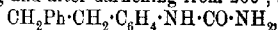
reaction a methylimino-product can be obtained. These substances also are possibly not homogeneous, and like iminoindigotin, exhibit both acidic and basic tendency.

D. F. T.

Syntheses in the Fatty Aromatic Series. X. Derivatives of Diaryl Paraffins. JULIUS VON BRAUN, (H. DEUTSCH, and O. KÓSCIELSKI (*Ber.*, 1913, **46**, 1511—1526).—Attempts to prepare definite substitution products of diaryl paraffins by sulphonation, chlorination, or nitration have been only partly successful, the compounds obtained showing little tendency to crystallise or to distil without decomposition; 4:4'-dicarboxylic acids have been prepared by the use of oxalyl chloride, but the corresponding amides do not yield any considerable quantity of amines when subjected to Hofmann's reaction. Further attempts to prepare symmetrically substituted dinitro-derivatives have met with slight success, but well characterised tetranitro-derivatives, $C_6H_3(NO_2)_2[CH_2]_x \cdot C_6H_3(NO_2)_2$, have been obtained.

A method of obtaining mono-substituted derivatives of diaryl paraffins consists in the condensation of acyl derivatives of chlorinated bases with benzene in the presence of aluminium chloride (compare A., 1912, i, 688), a reaction which is remarkable, since the corresponding nitro-derivatives appear to be unsuitable for the Friedel-Crafts reaction. If, however, the chlorine atom is in the δ - or ϵ -position with respect to the benzene nucleus, hydrogen chloride is almost entirely eliminated from within the molecule.

4-Benzoylaminodibenzyl, m. p. 170—171°, is obtained in almost theoretical yield by the condensation of *p*-benzoylaminophenylethyl chloride with benzene in the presence of aluminium chloride, and is readily transformed into *p*-aminodibenzyl, colourless leaflets, which are stable to light, m. p. 48°. The latter forms a *hydrochloride*, leaflets, m. p. 210° after darkening at 205°, a *platinichloride*, m. p. 286—289° according to the rate of heating and after darkening from 200°, a *carbamide*,



m. p. 155°, and a *phenylthiocarbamide*, m. p. 154°. The constitution of *p*-aminodibenzyl follows from its transformation into dibenzyl by the successive action of nitrous acid and stannous chloride. 4-Iododibenzyl, m. p. 44—45°, b. p. 210°/10 mm. (slight decomp.), reacts with sodium in much the same manner as does iodobenzene, but more slowly than the latter with copper powder or magnesium. 4-Hydroxydibenzyl forms yellow leaflets, m. p. 90°, and yields a yellow sodium salt with concentrated sodium hydroxide and a benzoyl derivative, m. p. 99°. Dibenzyl-4-carboxylonitrile is an oil which slowly solidifies when preserved, and is transformed by hydrochloric acid at 120° into dibenzyl-4-carboxylic acid, leaflets, m. p. 165°. The azo-dyes obtained from amino- and hydroxydibenzyl closely resemble those obtained from *p*-toluidine and *p*-cresol, so that the authors are led to the conclusion that the number of groups present is of greater importance for the alteration of colour than is the increase in weight of a group already present.

p-Nitrophenylethyl chloride, even after protracted treatment with benzene and aluminium chloride, yields oily products which still contain chlorine, and from which a uniform, chlorine-free nitro-

compound cannot be isolated. *p*-Nitrophenylpropyl chloride behaves in a similar manner.

p-Benzoylamino-phenylpropyl chloride condenses with benzene in the presence of aluminium chloride to yield an oily product, which, when hydrolysed by hydrochloric acid at 150°, gives a colourless, mobile base, b. p. 95–110°/17 mm., which is probably aminohydrindene,

$\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} > \text{CH}_2$ (benzoyl derivative, m. p. 161°), and *p*-amino-diphenylpropane, b. p. 210–225°/18 mm. (slight decomp.). The latter does not solidify when preserved during several months. It forms a picrate, benzoyl and *m*-nitrobenzoyl derivative, all of which are oily. The hydrochloride has m. p. 195°. When heated with methyl iodide (about 4 mols.) and sodium hydroxide, *p*-aminodiphenylpropane yields the corresponding quaternary iodide, $\text{Ph} \cdot [\text{CH}_2]_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_3\text{I}$, colourless needles, m. p. 179–180°, and *p*-dimethylaminodiphenylpropane, b. p. 221–222°/17 mm. The latter is best obtained in the pure state by decomposition of the quaternary iodide in a vacuum. *p*-Hydroxy-diphenylpropane has b. p. 215–220°/18 mm.

o-Aminodiphenylpropane, in contrast to the corresponding *p*-compound, yields a solid *m*-nitrobenzoyl derivative, m. p. 137°. Even with a large excess of methyl iodide it gives solely the tertiary amine, b. p. 177–183°/17 mm. (slight decomp.), which, although viscous, does not solidify.

p-Benzoylamino-phenylamyl chloride, m. p. 210–212°, reacts with benzene and aluminium chloride to yield a product, the nitrogen content of which is too high for a normal condensation product (see above).

Only minimal amounts of substance could be obtained by the condensation of acyl derivatives of chloro-bases with thiophen.

The action of oxalyl chloride on a solution of $\alpha\alpha$ -diphenylhexane in carbon disulphide in the presence of aluminium chloride results in the isolation of the dicarboxylic acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot [\text{CH}_2]_6 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, m. p. 303–304°, the potassium salt of which is sparingly soluble in water, whilst the sodium and ammonium salts are more soluble. The corresponding amide, m. p. 178°, like the diamide of diphenyloctane-dicarboxylic acid, is converted by bromine and alkali into a dark amorphous mass from which practically nothing can be extracted by acids.

Reduction of the oily product obtained by the nitration of diphenylhexane leads to a basic substance, which, when benzoylated, yields a benzoyl derivative of indefinite m. p. The latter may be resolved by alcohol into two isomeric portions, the less soluble of which, m. p. 212°, is probably mainly *pp'*-dibenzoylamino-diphenylhexane, and is converted by hydrochloric acid at 140° into a hydrochloride, $\text{C}_{15}\text{H}_{28}\text{N}_2\text{Cl}_2$, which melts indefinitely at about 205°. The more soluble portion has m. p. 174°.

It is noteworthy, that although the homologues of benzyl chloride readily condense in the presence of sodium with formation of diaryl paraffins, a similar reaction does not occur when the benzene nucleus contains a nitro- or benzoylamino-group.

The preparation of tetranitro-derivatives of diarylparaffins (compare Borsche and Wollemann, this vol., i, 171) is best effected by gradual addition of the hydrocarbon to nitric acid (D 1.52) at –15°. The

mixture is allowed to remain for half an hour in ice and then during two hours at the ordinary temperature, after which it is heated for a few minutes on the water-bath and then poured into water. In this manner diphenylhexane yields 2:4:2':4'-tetranitro- α - ζ -diphenylhexane, colourless needles, m. p. 90°, which, on oxidation with chromic acid, is converted into 2:4-dinitrobenzoic acid. Similarly, tetranitro- β - η -diphenyloctane, m. p. 145–146°, and tetranitro- α - ζ -diphenyl- β - ϵ -dimethylhexane, m. p. 112°, are obtained from the corresponding hydrocarbons. Reduction of 2:4:2':4'-tetranitro- α - ζ -diphenylhexane in ammoniacal alcoholic solution by means of hydrogen sulphide yields mainly dinitrodiaminodiphenylhexane, in which the two amino-groups are probably in the para-position to the hexamethylene chain. (Its hydrochloride was also examined.) Smaller quantities of trinitroaminodiphenylhexane, m. p. 126–127°, and of an isomeric dinitrodiaminodiphenylhexane, m. p. 150–151°, in which the amino-groups are probably in the ortho-position to the hexamethylene chain, are also formed. 2:4:2':4'-Tetra-aminodiphenylhexane, needles, m. p. 138°, is obtained by the reduction of 2:4:2':4'-tetranitrodiphenylhexane by tin and hydrochloric acid. The hydrochloride, m. p. 275°, picrate, needles, m. p. 213–215°, benzoyl derivative, which is not melted at 280°, and tetrabenzyldene derivative, m. p. 151°, were investigated. The base is converted by an excess of boiling acetic anhydride into its tetra-acetyl derivative, m. p. 270°; acetylation by glacial acetic acid, in the presence of a few drops of water, gives a diacetyl compound, leaflets, m. p. 167°.

Tetra-amino- β - η -diphenyloctane,

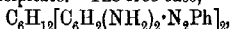


colourless leaflets, m. p. 131°, is obtained in a similar manner from the corresponding tetranitro-compound.

H. W.

Syntheses in the Fatty-Aromatic Series. XI. Double Dye-stuffs from Diarylparaffins. JULIUS VON BRAUN and O. KOSCIELSKI (*Ber.*, 1913, 46, 1526–1529).—The authors have investigated the effect of the repetition of one and the same chromophore in an organic molecule on the intensity and nature of the colour [compare preceding abstract]. They have prepared double dyes in the azo-, triphenylmethane-, indamine, and azine series, and do not find any noticeable difference between them and the corresponding mono-dyes.

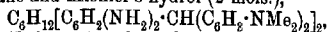
2:4:2':4'-Tetra-amino- α - ζ -diphenylhexane and tetra-amino- β - η -diphenyloctane when dissolved in dilute acid and treated with sodium nitrite yield reddish-brown colorations exactly similar to that given by 2:4-tolylene-diamine under similar conditions. On keeping, or immediately in concentrated solution, the "Vesuvius" separate as amorphous, dark brown powders which were not further investigated. When 2:4:2':4'-tetra-amino- α - ζ -diphenylhexane is treated with benzenediazonium chloride (2 mols.), the bis-chrysoidine separates as a red precipitate. The free base,



is a yellow, crystalline powder, m. p. 148–150°. The shades given by bis-chrysoidine and by the products derived from tolylenediamine

and tetra-aminodiphenyloctane are scarcely distinguishable from one another.

Tolylenediamine condenses with Michler's hydrol in acetic acid solution to yield the *base*, $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{C}_6\text{H}_4\text{Me}(\text{NH}_2)_2$, m. p. 156—158°. The corresponding *acetyl* derivative has m. p. 200°, and is oxidised by lead peroxide to a product which dyes cotton a pure green. The similar *leuco-base*, obtained from 2:4:2':4'-tetra-amino- α,α' -diphenylhexane and Michler's hydrol (2 mols.),

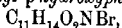


has m. p. 222°. With acetic anhydride it yields a *tetra-acetyl* derivative, m. p. 255—256°, which is oxidised by lead peroxide. The dye so obtained has precisely the same colour as that obtained from tollyenediamine in solutions of similar concentration, and yields precisely the same shades on cotton.

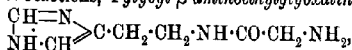
Amorphous *dyes* are obtained by the condensation of 2:4:2':4'-tetra-amino- α,α' -diphenylhexane or tetra-aminodiphenyloctane with nitrosodimethylaniline hydrochloride. These give blue colours on the fibres indistinguishable from those obtained with tollylene-blue. When an aqueous solution of these dyes is boiled, the colour changes to red. The "double-reds" so obtained dye the fibres in practically the same shades as tollylene red.

H. W.

Amines Derived from Proteins: The Peptamines Glycyl-*p*-hydroxyphenylethylamine, Alanyl-*p*-hydroxyphenylethylamine, and 4-Glycyl- β -aminoethylglyoxaline. MARKUS GUGGENHEIM (*Biochem. Zeitsch.*, 1913, 51, 369—387).—It is known that by the scission of carbon dioxide from certain amino-acids, such as tyrosine and histidine, bases of pharmacological interest are obtained. The author has consequently undertaken the investigation of similar products from peptides, and with this object has prepared synthetically the substances named above. By the action of chloroacetyl chloride on *p*-hydroxyphenylethylamine, *chloroacetyl-p-hydroxyphenylethylamine*, $\text{C}_{10}\text{H}_{12}\text{O}_2\text{NCl}$, m. p. 109°, is obtained, which by the action of aqueous ammonia yields glycyl-*p*-hydroxyphenylethylamine, $\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2$, m. p. 136°. By the action of bromopropionyl chloride on *p*-hydroxyphenylethylamine, *dl-bromopropionyl-p-hydroxyphenylethylamine*,



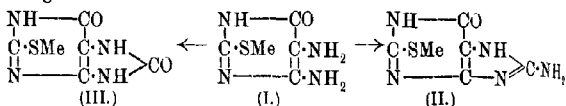
m. p. 98°, was obtained, which yields on treatment with ammonia *dl-alanyl-p-hydroxyphenylethylamine*, $\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_2$, m. p. 116°. By a similar series of reactions, *4-glycyl- β -aminoethylglyoxaline*,



was obtained, the hydrochloride of which melted with decomposition at 250°. The pharmacological action of these substances was investigated and compared with the actions of *p*-hydroxyphenylethylamine and 4- β -aminoethylglyoxaline. The conjugated products have a similar peripheral action on smooth muscle as the simple bases, but the effect is much weaker. The actions were investigated on the uterus, surviving small intestine, the frog's heart, etc., and on the blood-pressure, and the effects are illustrated by numerous tracings.

S. B. S.

Purines. X. 6:8-Dioxy-2-methylthiopurine and 8-Amino-6-oxy-2-methylthiopurine. CARL O. JOHNS and EMIL J. BAUMANN (*J. Biol. Chem.*, 1913, 14, 381—388).—The first orthodiaminoalkylthiopuridine has been prepared and condensed to a purine. The presence of the methylthiol group instead of sulphur modified the properties of the new compound, 4:5-diamino-6-methylthiol-6-pyrimidone (I). Instead of combining with thiocarbamide to form a thiopurine, as 4:5-diamino-2-thio-6-pyrimidone does (this vol., i, 657), it gave an aminopurine (II), which is accounted for by assuming that the thiocarbamide is first transformed into guanidine thiocyanate. The latter substance is, indeed, the best reagent to use for the preparation of the aminopurine, which may even be obtained by employing ammonium thiocyanate. This is remarkable in view of the fact that a similar condensation between other diaminopyrimidines and guanidine salts could not be realised.



4-Amino-2-methylthiol-6-pyrimidone (A., 1905, i, 836) is best obtained by using methyl sulphate instead of methyl iodide. When it is dissolved in water with sodium nitrite and then acidified with acetic acid, 5-nitroso-4-amino-2-methylthiol-6-pyrimidone, $\text{C}_5\text{H}_6\text{O}_2\text{N}_4\text{S}$, is precipitated as a white solid, which gives a blue solution in acids and a red in alkalis, and decomposes at 255° . It was reduced to 4:5-diamino-2-methylthiol-6-pyrimidone (I), by means of ammonium sulphide, only just sufficient to discharge the red colour due to the nitroso-compound being added. The substance was dried at $30\text{--}40^\circ$, and formed colourless crystals, m. p. 211° , which condense with carbamide to form 6:8-dioxy-2-methylthiopurine (III) as a granular powder which gives the murexide reaction, is unaltered at 320° , and hydrolyses with difficulty to uric acid. 8-Amino-6-oxy-2-methylthiopurine (II) is also stable at 320° , gives the murexide reaction, and is hydrolysed by acids but not by alkalis, to uric acid. J. C. W.

Action of Azoimide on Thiocarbimides and Carbimides. Constitution of Azoimide. V. E. OLIVERI-MANDALÀ and F. Noto (*Gazzetta*, 1913, 43, i, 304—315).—By the action of azoimide on ethylcarbimide the authors have obtained ethylcarbamazide, and from phenylcarbimide, phenylcarbamazimide, identical with that of Curtius and Hofmann (A., 1896, i, 648). From these results the authors consider it probable that azoimide and the azoimides should have the same structure, and they give reasons for preferring the cyclic formula

$\text{HN} \begin{array}{c} \diagup \text{N} \\ \diagdown \text{N} \end{array}$, for azoimide to the chain formula which has been suggested.

By the action of azoimide on phenylthiocarbimide, one of two substances is obtained according to the temperature of reaction; at 40° , one molecule of azoimide reacts, yielding 4-phenyl-3-thiotetrazoline of Freund and Hempel (A., 1895, i, 193), whilst at $60\text{--}70^\circ$ two molecules of azoimide are involved.

Ethylcarbamazoidime, $\text{NHEt}\cdot\text{CO}\cdot\text{N}_3$, prepared in ethereal solution, has b. p. $90^\circ/28$ mm., m. p. $10-14^\circ$; it forms large, tabular crystals. Its reactions are similar to those of other azoimides containing the group $\cdot\text{NH}\cdot\text{CO}\cdot\text{N}_3$. The action of water yields ethylamine azoimide, whilst alkalis yield ethylamine; the action of aniline on the substance leads to the formation of *s*-phenylethylcarbamide and aniline azoimide.

The action of azoimide on phenylthiocarbimide in ethereal solution is only complete at $40-50^\circ$ (under pressure). When the phenylthiotetrazoline produced is dissolved in warm xylene, a decomposition occurs and triphenylisomelamine, m. p. 190° , is obtained. Hofmann (A., 1886, 233) gave m. p. 185° . Triphenylisomelamine platinumchloride, $\text{C}_{21}\text{H}_{18}\text{N}_6\cdot\text{H}_2\text{PtCl}_6$, was also prepared.

When an ethereal solution of azoimide and phenylthiocarbimide is heated under pressure at $60-70^\circ$ for twenty-four hours, a substance, $\text{C}_7\text{H}_7\text{N}_7\text{S}$, is produced, which crystallises in soft, shining scales, m. p. $158-159^\circ$. When it is boiled with 50% potassium hydroxide, it yields azoimide and the thiocarbimide. Alcoholic sodium hydroxide eliminates 1 molecule of azoimide, yielding thiolphenyltetrazole, m. p.

150° . In view of these reactions the annexed structural formula is probable for the new substance.

R. V. S.

Supposed Isomerism of Benzeneazoresorcinol. ARTHUR HANTZSCH (*Ber.*, 1913, 46, 1556—1557).—Two isomeric forms of benzeneazoresorcinol have been described by Will and Pukall (A., 1887, 660). The product, m. p. 161° , is, in reality, a hydrate containing $\frac{1}{2}\text{H}_2\text{O}$, which can only be removed with difficulty. The dehydrated product has m. p. $169-170^\circ$, in agreement with that (170°) of the supposed isomeride. A very unstable *monohydrate* is obtained when acetic acid is added to a cooled alkaline solution of benzeneazoresorcinol.

II. W.

[Preparation of Aminoazo-derivatives of Aromatic *m*-Di-amines.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 258653).—It is found that 2:4-diaminophenetole, 2:4-diaminoanisole, or other ethers of 2:4-diaminophenols readily undergo bisdiazotisation by the ordinary methods, and when coupled with 2 mols. of a *m*-diamine (substituted or otherwise) furnish brownish-red compounds. 2:4-Diaminoanisole and 2:4-diaminophenetole form colourless needles with m. p. $67-68^\circ$.

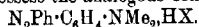
The nitro-ethers can be prepared as described by Willgerodt (A., 1879, ii, 716), and are readily reduced by the ordinary methods.

F. M. G. M.

Nature of the Yellow and Red Helianthine Solutions and Chromoisomerism of Aminoazo-salts. ARTHUR HANTZSCH (*Ber.*, 1913, 46, 1537—1556).—The solid, red helianthine is dissolved, not only by alkalis, but by all indifferent solvents in the form of yellow helianthine. Red helianthine solutions are only formed in the

presence of hydrogen ions. Yellow helianthine solutions are therefore obtained in the absence of hydrogen ions and not merely in the presence of hydroxyl ions.

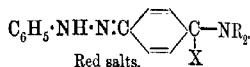
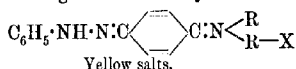
Yellow helianthines and red helianthines, as internal sulphonates, are optically very similar to the yellow and red chrmoisomeric salts of aminoazobenzenes with acids. The generally very unstable, yellow acid salts are optically quite distinct from the yellow salts of the type $N_2Ph \cdot C_6H_4 \cdot NMe_3X$, the absorption of which resembles that of azobenzene, and cannot therefore possess the analogous constitution



Since the quinonoid character of the red salts, $NHPh \cdot N : C_6H_4 : NR_2X$, is established by the analogy of their absorption with that of magenta the yellow salts must have the formula

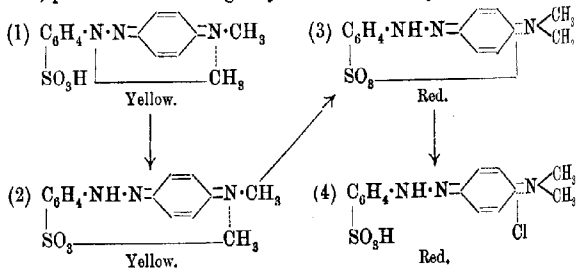


if structural isomerism is assumed. More probably, however, the yellow salts are themselves quinonoid, since they show a quinonoid band similar to that of the red salts and the aniline dyes, and hence must be regarded as valency isomerides of the red salts, thus:



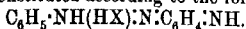
This conception leads to the adoption of a quinonoid structure for the corresponding aminoazobenzenes, $C_6H_5 \cdot N : N : C_6H_4 : NR_2$, since the latter yield spectra closely analogous to those of the yellow acid salts.

In a similar manner, the transformation of yellow methyl-orange into red helianthine probably takes place in the following stages: The yellow sodium salt present in the alkaline solution is transformed by neutralisation of the alkali into the corresponding free acid (1) which immediately passes into the yellow internal salt (2) by wandering of the hydrogen atom; this yellow helianthine is converted by acid into the red valency isomeride (3), which, in the presence of a large excess of acid, passes into the analogously constituted red hydrochloride (4).



Whilst the dialkylaminobenzenes, including the halogenalkylates, which are incapable of isomerisation yield three series of salts, the

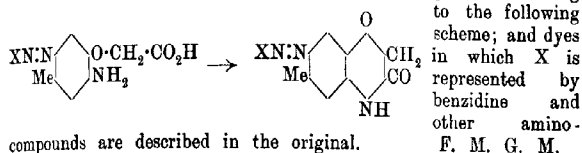
simple aminoazobenzenes can yield also a fourth graphite-black series which are possibly constituted according to the formula



Red helianthines are best obtained in the pure condition by means of their pyridine salts, which, when dried at 100° , lose pyridine, leaving the pure helianthine.

Ethyl dimethylanilineazobenzoate, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$, forms leaflets of a reddish-golden colour, m. p. 160° . H. W.

[Preparation of Compounds Containing 3:4-Dihydro-1:4-oxazine-3-one Ring.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 259700).—When the azo-compounds obtained from 1-amino-2-naphthoxyacetic acids or 2-aminophenoxyacetic acids which contain an alkyl or alkyl-oxy-group in the meta-position are treated with acids, they lose water and furnish cyclic compounds according



F. M. G. M.

Amount of *l*-Tyrosine in Proteins and the Accuracy of the Estimation of this Amino-acid. EMIL ABDERHALDEN (*Zeitsch. Physiol. Chem.*, 1913, 85, 91. Compare this vol., i, 409).—*l*-Hydroxyproline, like tyrosine, shows a blue coloration with the Folin-Denis reagent. The preparation used had $[\alpha]_D^{20} - 72.37^\circ$. A synthetic product made by Leuchs has $[\alpha]_D^{20} - 76^\circ$, whereas the value usually given is $[\alpha]_D^{20} - 81^\circ$. Since tryptophan and hydroxytryptophan also react with the Folin-Denis reagent, their method for estimating tyrosine is of no value. E. F. A.

The Oxidative Degradation of the Proteins. OTTO EISLER (*Biochem. Zeitsch.*, 1913, 51, 26—44).—On oxidation of proteins with calcium permanganate, "peroxyprotic" acids are produced, which, according to von Fürth, undergo hydrolysis with barium hydroxide with scission of oxalic acid, yielding deaminoprotic acids, which on further oxidation with permanganate yield "kyroprotic" acids. These, on treatment with barium hydroxide yield deaminokyroprotic acids. The deaminokyroprotic acid from caseinogen was prepared and described. The mercury salt contained 18.35% C, 2.62% H, 5.04% N, 0.4% S, 59.3% Hg, 1.7% amino-acid nitrogen (estimated by van Slyke's method), and 0.44% basic nitrogen. The probable constitution of this acid is discussed by the author. Sericoïn was also prepared from silk-waste by Weyl's method. This also was submitted to oxidation by calcium permanganate, and the product hydrolysed by barium hydroxide. The substance thus obtained could not be oxidised further by permanganate in the cold. The mercury salt contained 8.02% C, 1.06% H, 3.40% N, 12.85% O, and 74.67% Hg. The amino-acid nitrogen was 2.21%, and the basic nitrogen 1.72%. The high

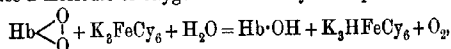
percentages of the latter and of the mercury are remarkable. They indicate that the simpler amino-acid groups are removed by oxidation, leaving the more basic groups intact, which seems to show that the protein is built up by branched chains from a more stable residue of diamino-acids. S. B. S.

The Amounts of Indole Produced by the Artificial Digestion or Putrefaction of Various Proteins. WACŁAW VON MORACZEWSKI (*Biochem. Zeitsch.*, 1913, 51, 340—354).—The amount of indole obtainable from various proteins by successive digestion with pepsin, trypsin, and putrefactive bacteria, both under the simplest conditions and in the presence of various foreign substances, such as fats, sugars, bile, etc., was estimated. The results are tabulated. S. B. S.

Hæmoglobin. The Magnesium Derivative of Mesoporphyrin. JEAN ZALESKI (*Ber.*, 1913, 46, 1687—1691).—In order to introduce magnesium into mesoporphyrin (compare Willstätter and Forsén, this vol., i, 499), the substance is treated with magnesium, methyl or ethyl iodide, and a trace of iodine in ethereal solution; the product is a compound, $C_{38}H_{46}O_3N_4Mg$, or $C_{39}H_{48}O_3N_4Mg$, m. p. 335°, which in its absorption bands and easy scission of magnesium on treatment with dilute acid closely resembles rhodophyllin (Willstätter, A., 1908, i, 198); the substance, m. p. near 288°, obtained by elimination of magnesium, is distinct from the ethyl ester of mesoporphyrin originally taken. D. F. T.

Methæmoglobin. BÉLA VON REINBOLD (*Zeitsch. physiol. Chem.*, 1913, 85, 250—285).—It is regarded as established that methæmoglobin takes a middle position between hydroxyhæmoglobin, $Hb\begin{smallmatrix} O \\ \diagup \diagdown \\ O \end{smallmatrix}$, and reduced hæmoglobin, Hb. It is uncertain whether it has Zeynek's formula $Hb(OH)_2$ or Küster's formula $Hb\cdot OH$.

It is now proved by spectrophotometric and gasometric measurements that the reaction between potassium ferricyanide and hydroxyhæmoglobin is quantitative, one molecule of the cyanide being required to displace a molecule of oxygen as shown by the equation



which is in agreement with Küster's formula.

E. F. A.

Keratin of White Human Hair. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1913, 85, 246—249).—The result of hydrolysing white human hair is as follows: Glycine, 9·12; alanine, 6·88; leucine, 12·12; glutamic acid, 8·0; phenylalanine, 0·62; tyrosine, 3·3, and cystine, 11·55%. The amounts of cystine, glycine, and alanine are abnormally large. Hair keratin closely resembles that from sheep's wool.

E. F. A.

Keratin of the Scales of *Manis japonica*. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1913, 85, 241—245).—The keratin of *Manis japonica* yields amino-acids on hydrolysis, namely, glycine 1·33%

alanine 120%, valine 4%, leucine 10.25%, proline 3.5%, glutamic acid, 3.5%, phenylalanine 2.67%, tyrosine 13%, and cystine 4.5%. The amount of alanine is abnormal, other keratins yielding 1.2%—1.8%. The proportion of tyrosine is likewise unusually large. E. F. A.

Keratin of Snake Skins (Boa Constrictor and Python). HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1913, 85, 335—340).—The distribution of the nitrogen and the percentage of certain monoamino-acids is determined in the keratin of snake skins, and compared with that in other keratins. The distribution of the nitrogen is much the same in all keratins, but they differ widely in the proportions of the individual amino-acids which they contain. Snake-skin keratin contains a high proportion of tyrosine and leucine. E. F. A.

Action of Quinones on Wool and Other Protein Substances. WILHELM FAHRION (*Zeitsch. angew. Chem.*, 1913, 26, 328. Compare *ibid.*, 1909, 22, 2138).—A claim for priority against Scharvin (this vol., i, 661). H. W.

Reactions on Dyeing Animal Fibres. WILHELM SUIDA (*Zeitsch. physiol. Chem.*, 1913, 85, 308—323).—Wool loses more of its substance in a faintly acid bath than in a neutral bath when heated under the conditions usual for dyeing. The difference is especially marked on subsequent treatment with an alkaline bath. Wool in both cases mainly gives up basic substances to the bath, so that, normally, during dyeing the wool itself becomes acid.

When wool is heated with phenols and acetic acid, the presence of the phenol on the fabric cannot be established, using ferric chloride. The substituted nitrophenols dye the wool, the intensity increasing with the acidity of the phenol. These colours are readily removed by faintly alkaline washes.

Wool fixes phenolcarboxylic acids, but no ferric chloride reaction is shown, indicating that the phenylhydroxyl group has combined with some constituent of the wool.

Whereas *p*-benzoquinone, toluquinone, *o*-3:6-xyloquinone, etc., in a weak acetic acid bath dye wool intensely, *p*-2:5- and *m*-2:5-xyloquinone, also thymoquinone, anthraquinone, and phenanthraquinone have no such action. The active para-quinones all contain the grouping $-\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{CO}-$, which is absent from the inactive quinones.

Naphthazarin, a dihydroxy- α -naphthaquinone, dyes wool a deep violet-brown. The colour is not removed even by strong ammonia.

The quinones are supposed to give rise to quinoneanilide-like compounds with the amino-substances of the wool. Silk is not dyed so quickly by quinones as wool. E. F. A.

Precipitation of Enzymes from their Solutions by Moist Aluminium Hydroxide. WILLIAM H. WELKER and JOHN MARSHALL (*J. Amer. Chem. Soc.*, 1913, 35, 822).—When solutions of the following enzymes were shaken with moist aluminium hydroxide, the enzymes were quantitatively removed: peroxydase and oxydase (aqueous extract of potato), pepsin (aqueous or 0.2% HCl solution), rennin

aqueous solution), trypsin (0.5% Na_2CO_3 solution, 30% alcoholic extract of pancreas, or 30% alcoholic extract of pancreas containing an equal volume of 1% Na_2CO_3), and amylase and lipase (30% alcoholic extract of pancreas). The amylase of saliva was not completely removed by this treatment; the filtrate was capable of converting starch paste into soluble starch, but could not effect further hydrolysis. Pepsinogen could be precipitated quantitatively, but only with great difficulty. E. G.

Action of Hydrogen Chloride and Ammonia Gas on Invertase. VI. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, 85, 225—230. Compare this vol., i, 113, 541, 662).—Invertase, when treated in turn with dry hydrogen chloride and dry ammonia, does not recover its hydrolytic activity. The groups destroyed by the acid are not restored when this is neutralised as is the case with diastase. This behaviour is regarded as further evidence in favour of the formation of anhydride by the action of the acid. E. F. A.

Action of Nitrous Oxide on Invertase. VIII. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, 85, 392—398).—On subjecting invertase to the action of dry nitrous oxide, oxidation takes place, and subsequently a little nitrous oxide is fixed by the enzyme. The hydrolytic activity of the enzyme is not affected. The treatment increases the acidity of the enzyme, although in one instance the acidity decreased. The amount of amide and amino-nitrogen is less after treatment. The experiments again emphasise the difference between invertase and diastase. E. F. A.

Action of Hydrogen Chloride and Ammonia on Diastase. V. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, 85, 97—111).—The action of dry hydrogen chloride and ammonia separately on diastase has already been studied (compare this vol., i, 113, 541). The enzyme has now been treated first with hydrogen chloride, and then with an excess of dry ammonia gas. The resulting increase in weight, acidity and nitrogen, shown by means of formaldehyde, was the same as when the enzyme was acted on by ammonia alone. The treatment with ammonia restores the hydrolytic activity of the diastase, whereas if the enzyme, after treatment with hydrogen chloride, is neutralised with aqueous ammonia, it remains inactive. E. F. A.

Action of Nitrous Oxide on Diastase. VII. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, 85, 292—307).—Dry nitrous oxide gas was passed over diastase in the manner described for hydrogen chloride or ammonia. Whereas an enzyme preparation containing milk sugar absorbed about 3% of the gas, a purified enzyme material absorbed three times this amount. Only a small quantity of the gas can be pumped off in a vacuum. The nitrous oxide does not cause either hydrolytic decomposition or anhydride formation. The hydrolytic activity of the purified enzyme is largely destroyed by the treatment, but the presence of the milk sugar protects the enzyme from harm. E. F. A.

Action of Salts of Metals on the Saccharification of Starch by Amyolytic Ferments. C. GERBER (*Bied. Zentr.*, 1913, 42, 265—268; from *Compt. Rend. Soc. Biol. Paris*, 1911, 70, 139, 391, 547, 724, 726, 728).—Alkali salts of monobasic acids increase the rate of saccharification when present in small amounts, whilst large amounts have a retarding effect; acid salts act similarly to the corresponding acids. The salts of monobasic organic acids act similarly; the retarding effect increases with the mol. wt.

Magnesium salts in small amounts have no action, and larger amounts have a retarding effect. Manganese, ferric and aluminium salts have a quickening effect in small amounts, and a retarding effect when present in large quantities. Ferrous salts retard or inhibit saccharification according to the amount.

Cadmium and zinc in very small amounts have a retarding effect, whilst moderate amounts inhibit saccharification. Still larger amounts, up to a certain point, are, however, favourable. Similar results were obtained with copper and gold salts.

Salts of platinum and palladium in very small amounts are favourable; the action is very suddenly reversed as the amounts increase.

N. H. J. M.

Synthesis of Glucosides of the Alcohols by means of Emulsin; Reversibility of Ferment Actions. ÉMILE BOURQUELOT and MARC BRIDEL (*Ann. Chim. Phys.*, 1913, [viii], 28, 145—218).—A résumé and discussion of results already recorded in the following abstracts: 1906, ii, 386; 1911, i, 1053; 1912, i, 522, 592, 593, 672, 733, 790, 928, 946; this vol., i, 212, 303.

T. A. H.

Behaviour of Emulsin in Presence of Pyridine. GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1913, 85, 415—426).— β -Glucosides are hydrolysed by emulsin in presence of 12% of pyridine. When the proportion of pyridine is increased, hydrolysis is retarded, and ceases in 20% solution. In presence of pyridine, amygdalin is converted into isomamygdalin.

E. F. A.

Use of Increasing Proportions of Dextrose in the Biochemical Synthesis of β -Methylglucoside. Influence of the Glucoside Formed on the Arrest of the Reaction. ÉMILE BOURQUELOT and ÉM. VERDON (*Compt. rend.*, 1913, 156, 1638—1640; *J. Pharm. Chim.*, 1913, [vii], 7, 575—579).—In methyl alcohol (70%) the quantity of glucoside formed increases proportionately as the quantity of dextrose in solution increases up to 12%, above which the amount of glucoside formed diminishes slightly. The presence of methylglucoside in the solution has a marked inhibiting effect on the amount of glucoside synthesised. The quantity of glucoside necessary to check the reaction is proportional to the amount of dextrose in the solution.

W. G.

Enzyme Action. XIX. Urease. II. Observations on Accelerative and Inhibitive Agents. HENRY E. ARMSTRONG, M. S. BENJAMIN, and EDWARD HORTON (*Proc. Roy. Soc.*, 1913, B, 86, 328—343. Compare A., 1912, i, 594).—The manner in which the

activity of urease is affected by the presence of various substances together with the urea has been studied throughout the whole course of the change with considerable accuracy. The results are expressed graphically.

Both strong acids and carboxylic acids such as *M/50* aspartic and salicylic acids prevent action. Boric acid in all strength retards action. Guaiacol and resorcinol at first retard and subsequently accelerate hydrolysis. *p*-Benzoquinone is poisonous, and quinol and quinol monomethyl ether, both of which are easily oxidised to *p*-benzoquinone, soon stop action. Glycine, asparagine, and carbonic acid all accelerate action.

It is emphasised that in presence of carbonic acid the rate of change approximates to a "linear" character.

Hydrogen cyanide accelerates action.

Saligenin, acetaldehyde, benzaldehyde and salicylaldehyde are moderately active depressants.

It is considered that enzymic changes would be found to take place at approximately constant rates were it not that they are subject directly and indirectly to considerable retardation by the products of change; probably the products of change have an affinity for the enzyme which is actually greater than that which obtains between the hydrolyte and the enzyme.

Enzyme action takes place entirely at the surfaces of colloid particles suspended in the solution of the hydrolyte, and not between substances which are all in true solution.

E. F. A.

Fermentations with Yeast in the Absence of Sugar. XI. Carboxylase. CARL NEUBERG and P. ROSENTHAL (*Biochem. Zeitsch.*, 1913, 51, 128—142).—The carboxylase from yeast, which causes the decomposition of pyruvic acid, can be distinguished from the sugar ferment (zymase) by various reactions. The latter does not act in the presence of chloroform, whilst the former retains its full activity, especially in the presence of "buffers," which prevent great changes in the reaction of the fermenting liquid. For this latter purpose, solutions of either alkali salts of pyruvic acid in the presence of free arsenious or boric acids or free pyruvic acid in the presence of borates or arsenites can be used. Similar results were obtained both with fresh and dried yeasts of pure culture. The carboxylase acts in a much shorter time than the zymase. Furthermore, if maceration juices are preserved at room temperature, the zymase activity is readily lost, whereas the carboxylase remains active over comparatively long periods. Furthermore, the zymase is readily destroyed by heating to 50°, whereas the carboxylase activity remains intact. There is a further difference in that the zymase loses its activity on dialysis, whereas the carboxylase does not, especially if the dialysed solution is kept for some time. Attention is called to the fact that the fermentation of sugar must precede in stages, the C_6 -sugar being apparently broken down into C_3 substances, such as pyruvic acid. The ferment causing the evolution of carbon dioxide from the latter can remain intact, even after the zymase is destroyed.

S. B. S.

Paralysis and Activation of Zymase and Catalase. HENRI VAN LAER (*Centr. Bakt. Par.*, 1913, ii, 37, 529—534. Compare A., 1912, i, 1043).—In an earlier paper it was stated that the addition of papain depresses, and malt extract increases, the activity of zymase and catalase. The former is attributed to impurities in the juice of the *Carica papaya* which digest the two enzymes.

The activation of the enzymes by extract of malt may be due, firstly, to direct stimulation of the zymase and catalase by impurities in the extract of malt; secondly, by inhibition of the antagonistic enzyme (protease) by impurities, or else to the existence of pro-enzymes—zymase and procatalase—combinations of the enzymes with a carbohydrate, such compounds being saccharifiable by amylase.

Experiments with a Munich bottom yeast and a Mons top yeast have been made, and again show a depressing action of the papain on the catalase and zymase in the yeast juice. Tests with extract of malt exhibit activation of the enzymes during the initial stages of the experiment with a pronounced depression later on. This action is ascribed to the presence of proenzymes in the yeast-juice. At the moment of fission a positive effect is produced, and this is followed by their digestion by impurities in the malt extract. H. B. H.

Arseno-compounds. AUGUST MICHAELIS and ARTHUR SCHÄFER (*Ber.*, 1913, 46, 1742—1743).—Since arsenic compounds frequently have a higher molecular weight than the corresponding nitrogen compounds, the authors have determined the molecular weight of arsenobenzene and *p*-arsenotoluene respectively.

Arsenobenzene, slender, white needles, has m. p. 212° , not 196° as previously given (A., 1881, 722). It is readily oxidised in solution to phenylarsine oxide, which, even in small quantities, greatly depresses the m. p. A solution of arsenobenzene in benzene, when allowed to evaporate spontaneously in contact with air, leaves a resinous product consisting solely of phenylarsine oxide. In boiling benzene solution, arsenobenzene has mol. wt. at 399.8 (calc. 304).

p-Arsenotoluene separates from benzene in small plates, m. p. 202° (from chloroform, however, in needles, m. p. 184° ; compare A., 1902, i, 411). In solution, it is readily oxidised to *p*-tolylarsine oxide. It has a normal molecular weight when dissolved in dry phenol. In the presence of a trace of moisture, on the other hand, a constant freezing point of the solution is not observed. H. W.

The Displacement of Metals from their Phenyl Compounds. SIEGFRIED HILPERT and GERHARD GRÜTTNER (*Ber.*, 1913, 46, 1675—1691).—Although the action of various metals on the organo-metallic compounds has been fairly well investigated in the aliphatic series, the corresponding behaviour with the compounds of the phenyl series has been less well studied (compare Hilpert and Grüttner, A., 1912, i, 939). It is now discovered that at the temperature of the experiment (200 — 350°) the metals of comparatively low m. p. generally react with the organo-metallic compounds causing a displacement of the other metal, and that if the two metals do not affect one

another the reaction may proceed quantitatively. If the m. p. of the resulting mixture of metals lies below the temperature of the experiment the extent of the interaction appears to be dependant on the relative quantities of the two metals in the mixture.

Magnesium and aluminium react with mercury diphenyl so readily that no external heating is necessary; magnesium diphenyl (compares Fleck, A., 1893, i, 622) does not inflame in the air unless breathed upon; it forms feathery needles (from ether), which melt at the temperature of the hand, almost immediately afterwards passing into the ether-free, amorphous substance. For the reaction between zinc and mercury diphenyl (in a hydrogen atmosphere), heat has to be applied when the chemical change occurs with quantitative displacement of mercury; zinc diphenyl, needles, m. p. 105—106°, b. p. 280—285°, both in hydrogen, is very sensitive to air and moisture, the former converting it into zinc oxide and diphenyl, and the latter into zinc hydroxide and benzene; it is inflamed by fuming nitric acid, and reacts with chloroform, producing triphenylmethane; with iodine in benzene solution it produces zinc phenyl iodide, which is slowly converted further into zinc iodide; with mercury it reacts to a small extent, giving a trace of mercury diphenyl.

Contrary to expectation, aluminium reacts scarcely at all with zinc diphenyl, possibly on account of the protecting film of oxide; in order to determine the relative reactivity of these two metals towards the metallic phenyl compounds, the two metals were allowed to react simultaneously with the same quantity of mercury diphenyl under such conditions that the zinc if alone would form zinc diphenyl; it was found that the relative amounts of aluminium triphenyl and zinc diphenyl were 99:1. Magnesium decomposes completely the phenyl derivatives of aluminium and zinc, whilst mercury has no effect on them; the metals magnesium, aluminium, zinc, and mercury, therefore, stand in the same relative order of activity as in the ordinary potential series.

Cadmium exhibits but little tendency to form organo-metallic compounds and with the mercury alkyls gives rise only to hydrocarbons; with mercury diphenyl it is found that cadmium reacts, forming cadmium diphenyl, but the extent of the reaction depends on the composition of the liquid cadmium amalgam produced, and therefore on the relative amount of cadmium applied; by using an apparatus in which the liquid reaction product could be repeatedly treated in a hydrogen atmosphere with fresh cadmium until more than ten atomic proportions had been applied, a specimen of *cadmium diphenyl*, colourless prisms containing 25% of mercury diphenyl, was obtained; it is stable when dry, but in benzene solution it undergoes atmospheric oxidation. From the amount of cadmium necessary in the above experiment and the fact that the product when heated with excess of mercury quantitatively regenerates mercury diphenyl, it is evident that cadmium falls after mercury in the series, showing the relative activity of the metals towards the formation of phenyl compounds.

The behaviour of bismuth is somewhat analogous to that of cadmium; mercury diphenyl heated with an excess of bismuth and bismuth triphenyl heated with an excess of mercury both yield a mixture of

the phenyl derivatives of the two metals; the relative proportions in the mixed products indicate that bismuth falls before mercury in the series indicating relative activity in these compounds. With the six metals investigated above, therefore, cadmium alone falls into a position different from that occupied in the ordinary potential series.

The quadrivalent metals lead and tin appear to form a special class, for they fail to react with mercury diphenyl, whilst their tetraphenyl derivatives are entirely unaffected by magnesium.

The behaviour of the metallic haloids towards metallic phenyl compounds is very different from that of the corresponding free metal. Mercuric bromide reacts quantitatively with an ethereal solution of magnesium phenyl bromide producing *mercury phenyl bromide*, leaflets, m. p. 375°, if the original reagents are in approximately equimolecular proportions; with an excess of the organo-magnesium compound, mercury diphenyl is formed, but in only 40% yield. In a similar manner, mercury α -naphthyl bromide, m. p. 202°, can be produced, which even with a large excess of magnesium α -naphthyl bromide gives only a small quantity of the diphenyl compound. Cadmium chloride also reacts with magnesium phenyl bromide and magnesium α -naphthyl bromide, but the products were not isolated.

It is remarked that the sensitiveness of the phenyl compounds towards air and water diminishes with increasing atomic weight and electro-negative character of the metal.

The action of the alkali metals on mercury diphenyl or zinc diphenyl, with or without a solvent, was never found to yield a deposit of mercury until water was added (compare Acree, *A.*, 1903, i, 724), and it is believed that an additive product is first produced.

In agreement with the earlier negative results (Smith, Barnett and Hall, *A.*, 1900, i, 89) on the existence of a tungsten methyl iodide (Cahours, 1862), the authors were unable to isolate any compound of such nature.

D. F. T.

Physiological Chemistry

Narcosis. I. The Relationship between Narcosis and Oxygen Respiration. HANS WINTERSTEIN (*Biochem. Zeitsch.*, 1913, 51, 143—170).—The author gives a critical review of the various experiments which indicate a relationship between narcosis and diminution of oxygen respiration. He draws the conclusion that narcosis cannot be explained simply as a result of diminished oxidation, citing amongst other experiments the fact that certain ascarids, which are anoxybiotic, are particularly susceptible to narcosis. It seems more probable that narcosis and inhibition of oxidation are concomitant results of some more general action.

S. B. S.

The Chlorine Content of Blood and its Division between the Corpuscles and Serum. **The Permeability of Corpuscles for Inorganic Substances.** J. SNAPPER (*Biochem. Zeitsch.*, 1911, 51, 53—61).—The chlorine was estimated in the total blood, and in the serum and corpuscles separately. It was found that the ratio of the chlorine in the corpuscles to that in the serum was approximately constant both in the dog and in man, being about 40%. As this is very nearly the ratio of the intraglobular fluid to the total volume of the erythrocytes as found by Hamburger, the conclusion is drawn that there is an even distribution of the inorganic contents of blood between the serum and the formed elements. S. B. S.

Formation of Methæmoglobin. WOLFGANG HEUBNER (*Arch. exp. Path. Pharm.*, 1913, 72, 241—281).—Whereas the injection of phenacetin into the blood of carnivora causes the formation of methæmoglobin, dimethylphenacetin is without effect. Phenacetin outside the body has no action on blood, indicating that the active substance is formed from it in the organism.

Parallel experiments with derivatives of *o*-, *m*-, and *p*-aminophenols show the meta-derivatives to be barely poisonous, and, whereas the ortho- and para-derivatives are equally poisonous for dogs, the ortho-compound is the stronger in the case of cats, which are extremely sensitive to both aminophenols. Rabbits are resistant to these poisons.

Since each aminophenol molecule reacts several times with hæmoglobin molecules, the reaction is explained on the hypothesis that the *o*- and *p*-aminophenols are oxidised to *o*- or *p*-benzoquinone-imine, and that this actually reacts with hæmoglobin, 2(Hb.Fe), forming aminophenol and methæmoglobin, 2(Hb.Fe.OH). The change involves conversion of bivalent into tervalent iron, the active agent being the quinone. This is in agreement with the formation of hæmoglobin by the agency both of oxidising and reducing agents.

Quinol acts similarly, but has no effect in the absence of oxygen. *p*-Benzoquinone works energetically in the absence of oxygen.

Quinol and catechol readily produce methæmoglobin in test-tube experiments, whereas resorcinol is without effect. Similarly, pyrogallol is active, chloroglucinol inactive.

Aniline is active, dimethylaniline has no effect, although the isomeric *m*-xylylidine is also active in producing methæmoglobin.

The substitution of the para- and of both ortho-positions in aniline by chlorine does not alter its activity. Apparently the aniline nitrogen is oxidisable without oxidation previously taking place at the ortho- or para-positions in the nucleus to form a quinone. Acetylation of the nitrogen in trichloroaniline has little effect; in dichloroaniline some lessening of the activity is brought about on acetylating.

Hæmoglobin is oxidised by hydroxylamine even in the absence of oxygen. The introduction into aniline derivatives of two methyl groups occupying the one the ortho-position to nitrogen, and the other either the ortho- or para-position lowers the oxidising

activity. Phenetidine, for example, has hardly any action in producing methæmoglobin.

Emphasis is laid on the difference between rabbits, dogs, and cats in the reactions between the blood and aromatic oxidising agents.

The spectrum of pure methæmoglobin does not show the two oxyhæmoglobin bands in the yellow and green. When these are seen, oxyhæmoglobin is present as impurity. E. F. A.

The Change in the Permeability of Blood Corpuscles on Addition of Acid. J. SNAPPER (*Biochem. Zeitsch.*, 1913, 51, 62—88).—The results of Hamburger are confirmed, according to which the addition of acid causes a swelling of the corpuscles and a passage of chlorine from the serum into the corpuscles. The influence of the addition of acids to the blood both *in vivo* and *in vitro* was investigated. The diffusible and non-diffusible alkali was estimated. For this purpose, the total serum was titrated with *N*/25-tartaric acid, and also the filtrate after precipitation with alcohol, which throws down the proteins with the alkali combined with proteins (non-diffusible alkali). Congo-red paper was used as indicator. Both *in vivo* and *in vitro*, there was found to be a relative increase of the diffusible as compared with the non-diffusible alkali as a result of the action of acids. A possible explanation of the action of acids as regards the distribution of chlorine between serum and corpuscles seemed therefore to be the relative increase of $\cdot\text{SO}_4$ ions in the corpuscles when sulphuric acid was employed, as compared with the serum, due to the larger amount of alkali set free from proteins in a diffusible form and a subsequent interchange of $\cdot\text{SO}_4$ and Cl ions between serum and corpuscles. As, however, a change in distribution of chlorine could not be brought about by addition of neutral sulphates alone without addition of acids, this explanation is inadequate. It is assumed, therefore, that the acids act on the proteins and so alter the permeability of the cells to ions. A similar change of distribution could not be brought about by lipid solvents, such as chloroform, even when the latter is present in sufficient quantities to cause a small amount of hæmolysis. S. B. S.

The Biological Significance and Metabolism of the Proteins. VII. The Amino-Nitrogen Titratable in the Presence of Formalin in the Blood Corpuscles of Various Animals. A. COSTANTINO (*Biochem. Zeitsch.*, 1913, 51, 91—96).—The proteins were separated by barium salts by the method of Buglia and Costantino. In both the serum and corpuscles, nitrogenous substances titratable in the presence of formalin were found. The quantity found was small in the case of serum, but relatively large in that of corpuscles. In non-nucleated, the quantity is only about half that existing in nucleated corpuscles. In the case of mammals and turkey, the amount found in the serum is about the same. The author calls attention to the importance of examining chemically the corpuscles when investigating various problems of metabolism. S. B. S.

Hæmolysis by Chemical Agents. PHILIPP EISENBERG (*Centr. Bakt. Par.*, 1913, i, 69, 173—225).—The author has carried out a long series of experiments on the action of salts, acids, alkalis, and various organic substances (including tetanolysin and vibriolysin) on blood corpuscles. He has investigated, amongst other factors, the influence of hypertonicity, synergism, and antagonism. He summarises his results, from which, however, no extensive generalisations can be made. S. B. S.

Blood Lipoids and Phagocytosis. B. STUBER (*Biochem. Zeitsch.*, 1913, 51, 211—233).—A method is described by means of which the phagocytic index of leucocytes can be determined, thrush spores being employed as the foreign object, as they can be readily stained by Leishmann's method. For *in vitro* experiments human blood was employed, and for *in vivo* experiments cats and sometimes rabbits were used. It was found that cholesterol by itself greatly diminishes the phagocytic index, whereas lecithin has no action. On the other hand, lecithin greatly diminishes, and even obliterates when in sufficient quantity, the power of cholesterol to reduce the phagocytic index, provided that it has not been previously heated. If the cholesterol and lecithin are heated after mixing, they do not together diminish the phagocytic index. Similar results were obtained by both the *in vivo* and *in vitro* experiments. It appears, therefore, that cholesterol acts directly on the phagocytes, and destroys their phagocytic action, but in the presence of lecithin a lecithin-cholesterol compound is formed. This cannot, however, be produced if lecithin is heated before the two substances are mixed. S. B. S.

The Acetonitrile Reaction. FR. PORT (*Biochem. Zeitsch.*, 1913, 51, 224—228. Compare Reid Hunt, A., 1905, ii, 847; 1910, ii, 736; Trendelenburg, A., 1911, ii, 50).—The author throws doubt on Reid Hunt's acetonitrile reaction with mice for detection of thyreogenic substances in the blood on the ground that the susceptibility of the animals to the poison is so very variable that it is impossible to determine the limiting dose. S. B. S.

Influence of Fatigue on the Amount of Dialysable Compounds, which React with Triketohydrindenhydrate, in the Serum. EMIL AEDERHOLDEN and ARNO ED. LAMPÉ (*Zeitsch. physiol. Chem.*, 1913, 85, 136—142).—After severe fatigue in the dog, the blood-serum contains less of the substances referred to in the title. Admixture of the serum either of normal or fatigued dogs with cooked muscle produced no change. A similar result was obtained with other tissues. W. D. H.

The Fermentative Properties of Blood. I. A Peptolytic Ferment of Normal Dog's Serum. LUDWIG PINCUSOHN (*Biochem. Zeitsch.*, 1913, 51, 107—115).—It is known that by injection of various proteins into animals, the blood acquires peptolytic properties. The author shows that normal dog's serum

possesses a ferment capable of hydrolysing the peptone of dog's muscle, prepared by treating the muscular tissue with 70% sulphuric acid in the cold, and precipitating by alcohol, after the removal of the sulphuric acid with barium hydroxide. The serum does not, however, digest a similar peptone prepared in the same way from cat's muscle, or other peptones from foreign substances.

S. B. S.

The Influence of Diet on the Activity of Ptyalin. H. VAN TRICHT (*Zeitsch. physiol. Chem.*, 1913, 85, 156—160).—The author examined his saliva at frequent intervals; each meal increased its diastatic activity; the increased action was greatest after a carbohydrate meal, and least after a protein meal.

W. D. H.

Fluorine in the Animal Organism. II. Skeleton, Cartilages, and Tendons. ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1913, 156, 1425—1430. Compare this vol., i. 677).—An examination of bones, teeth, cartilage, and tendons for fluorine. Bones and teeth, either human or animal, are comparatively rich in fluorine, the content of the diaphyse portion of the bones being about four times as great as that of the epiphyse, in the case both of an elderly man and a new-born infant. The teeth approach the diaphyse in fluorine content. The skeleton of fish contains practically the same amount of fluorine as the scales, and a complete analysis of these organs shows a marked analogy. Cartilage and tendons are very low in fluorine content.

W. G.

Is it Possible Artificially to Increase the Amount of Phosphatides in Brain? ERNST SALKOWSKI (*Biochem. Zeitsch.*, 1913, 51, 407—422).—Commercial preparations of kephalin, when administered by the mouth, are well tolerated, and all but a small percentage is resorbed. Its ingestion causes an increased phosphoric acid output in the urine, both absolute and relative as compared with the nitrogen. In contrast to egg-yolk lecithin, kephalin does not accumulate in the liver, but appears to accumulate in the brain. Rabbits were used for the experiments, and the quantities of phosphatides in the organs were estimated by the following method. The organ (brain) was first extracted with hot alcohol, and the residue was then extracted with a mixture of equal volumes of absolute alcohol and benzene. The residues from both extracts were then dissolved in benzene, the extract thus made was filtered, and the phosphorus was estimated in the filtrate after the solvent had been evaporated off.

S. B. S.

Normal and Pathological Alteration in the Lens of the Eye. ADOLF JESS (*Zeitsch. Biol.*, 1913, 61, 93—142).—During life there is an increase in the weight, the protein, and the water of the crystalline lens, and to a smaller degree in the substances which are soluble in ether. The increase in protein is greater than that in water. Among the proteins, an "albumoid" is more abundant in old age than crystallin, which is the more important in youth.

VOL. CIV. i.

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In senile cataract, the weight, the water, and the protein all decrease, and the loss of water is greater than that of protein; among the proteins crystallin is most diminished; the amount of albumoid is high; the amount of fat, cholesterol, and lecithin are not increased. In traumatic cataract there is no decrease in weight, but both the proteins decrease in amount; fat, cholesterol, and lecithin do not increase, but the relative and occasionally the absolute amount of water usually rises. In senile cataract, the cystine reaction lessens owing to the disappearance of crystallin; the albumoid has no cystine group in its molecule. In old traumatic cataracts the cystine reaction is also negative, owing to the total absorption of crystallin.

W. D. H.

Chemical Investigation of Calcified Aortæ. FRANZ AMESDENER (*Zeitsch. physiol. Chem.*, 1913, 85, 324—334. Compare A., 1911, ii, 219).—A further series of analyses of calcified aortæ are given with full details of the experimental methods.

E. F. A.

A Pigment in Melanosis of the Mucous Membrane of the Large Intestine. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1913, 85, 92—95).—A brown pigment was separated from a melanotic large intestine. An elementary analysis is given, which agreed closely with that of a pigment obtained from tryptophan (A., 1912, i, 521).

W. D. H.

Ferments of the Pancreas. CESARE SERONO and ANTONIETTE PALOZZI (*Chem. Zentr.*, 1913, i, 1212—1213; from *Arch. Pharmacol. experim.*, 1913, 14, 501—508).—All the ferments of the pancreas are contained in the glycerol extract, expressed under high pressure, and their activity remains for a long time unimpaired. The proteoclastic activity increases on keeping, that is, with the conversion of trypsinogen into trypsin. In addition to diastase, there is a ferment capable of acting on maltose. The tryptic power is not destroyed by digestion with pepsin. Only the proteoclastic ferment is precipitated by a mixture of sodium chloride and magnesium sulphate.

S. B. S.

Autolysis of the Thymus. M. KASHIWABARA (*Zeitsch. physiol. Chem.*, 1913, 85, 161—172).—Kutscher considered that during autolysis the thymus underwent characteristic changes, especially in the amount of lysine and ammonia formed; the present research does not support this view. The course of autolysis in this organ does not materially differ from that of the liver, and there is no increase in the amount of ammonia formed; in both organs its nitrogen is about 10% of that in the soluble nitrogenous substances. Among the decomposition products, lysine was found, also leucine and tyrosine in small quantities. There are certain differences between liver and thymus in the partition of nitrogen; the mono-amino-acids and proteoses are only about half as abundant in the thymus as in the liver, but the group diamino-acids + peptone + ammonia is twice as great, and the purine bases three times as great.

W. D. H.

Extractive [Mytilitol] in the Valve Muscles of *Mytilus edulis*. BAREND C. P. JANSEN (*Zeitsch. physiol. Chem.*, 1913, 85, 231—232).—On extraction of the valve muscles of *Mytilus edulis* with water and precipitation of certain impurities with colloidal ferric hydroxide, a substance, $C_6H_{12}O_5 \cdot 2H_2O$, crystallises from the filtrate; the name *mytilitol* is applied to it. It forms an *acetate*, m. p. 182°, crystallising in microscopic needles, which gives up five acetyl groups on hydrolysis. Mytilitol contains a six-carbon ring, and is regarded as an isomeride of quercitol. The muscles also contain histidine, betaine, taurine, and about 1.5% of glycogen.

E. F. A.

The Influence of Nutrition on the Secretion of Indole and Indican by Healthy Individuals. WACLAW VON MORACZEWSKI and E. HERZFELD (*Biochem. Zeitsch.*, 1913, 51, 314—339).—The amount of substance giving the indole reaction, which is obtained by the distillation of urine, was determined under different conditions of nutrition, and it was found that the amount increased on a diet of fats, of vegetables, and of gelatin, but diminished on a carbohydrate or sugar diet. The addition of proteins caused an increased output as compared with sugars, but a diminished output as compared with fats. No relationship could be found between the indole of the faeces and the indican of urine. The indole of the faeces was estimated both directly as excreted, and after submission to a secondary putrefaction. Fat was found to increase both the indole directly excreted and the amount obtained after secondary putrefaction. The same was found with proteins, whereas carbohydrates had the opposite effect. Vegetables protect proteins from putrefaction, so that the indole directly excreted is diminished, and that obtained by secondary putrefaction is increased to the same extent. The nitrogen and chloride of the faeces are affected in a similar way. At times a relationship between the indican of the urine and the indole of the faeces is to be found, the two rising and falling together; in the case of gelatin, sugar, and fat nutrition, the general metabolism exerts some influence on the amount of indole resorbed from the intestine; but the amount of indican of the urine is regulated by another factor in addition to its resorption from the alimentary tract, namely, the capacity of the organism to destroy the absorbed substance.

S. B. S.

Tryptic Digestion by the Urine. FILIP JOHANSSON (*Zeitsch. physiol. Chem.*, 1913, 85, 72—90).—In the normal urine of man, ox, and horse, no proteolytic enzyme precipitable by caseinogen in an alkaline solution was obtained. In albuminous urine, it is sometimes present. From the urine of the ox, and to a small degree of the horse, the caseinogen precipitate contains an enzyme which favours the proteolytic action of fibrin prepared from ox blood, but has no such action on ox-serum. Trypsinogen is absent from the urine. The substance in question is possibly a kinase.

W. D. H.

Excretion of Glycuronic Acid Mistaken for Glycosuria. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1913, 85, 95—96).—A case of apparent glycosuria in a child turned out on further examination to have no sugar in the urine. The reducing properties were due to free and combined glycuronic acid. The urine also contained abundant phenol and indoxyl.

W. D. H.

Changes in Voluntary Muscles in Disease. R. C. JEWESBURY and W. W. C. TOPLEY (*J. Path. Bact.*, 1913, 17, 432—453).—In wasting diseases the voluntary muscles show varying degrees of wasting. In acute general diseases there is a hyaline or granular change, and in a few cases fatty degeneration. In cases of abnormal carbohydrate metabolism the interstitial fat is increased. Marked fatty degeneration occurs in diphtheritic toxæmia, certain blood disorders, and phosphorus poisoning. Glycogen was strikingly present in all the cases (three in number) of diabetes examined. Amyloid degeneration was not found at all.

W. D. H.

Biochemistry of Growth. The Glycogen-content of the Liver of Rats Bearing Malignant New Growths. WILHELM CRAMER and JAMES LOCHHEAD (*Proc. Roy. Soc.*, 1913, B, 86, 302—307).—Glycogen disappears more rapidly from the liver of tumour-bearing rats than from that of normal rats. There is no increased oxidation of carbohydrate material in tumour-bearing animals, so the result confirms the conclusion arrived at on pregnant animals, that in growth carbohydrate is used in the synthesis of protoplasm.

W. D. H.

Nitrogen Content of Malignant Tumours in Man. ROBERT G. CHISHOLM (*J. Path. Bact.*, 1913, 17, 606—608).—Ten tumours were investigated; in all cases the nitrogen percentage is lower in the fresh tumour than in the somatic tissues of the host, with the exception of the kidney. But reckoned for the dried tissue, the percentage was lower in four cases only. Cramer and Pringle found that the percentage of nitrogen coagulable by alcohol was low in tumour tissue; the variable results on this point obtained in the present research appear to be due to post-mortem changes.

W. D. H.

Action of Diuretics in Experimental Nephritis. ARTHUR E. BOYCOTT and JOHN H. RYFFEL (*J. Path. Bact.*, 1913, 17, 458—501).—After the convoluted tubules are put out of action by uranium nitrate, secretory diuretics, such as caffeine, fail to produce diuresis; so also do mechanical diuretics, such as Ringer's fluid. In the early stages of uranium nephritis, the urine produced is small in amount, and contains less chlorides than normal. Caffeine urine contains less chlorides than that produced by Ringer's solution or 5% sodium chloride solution. Uranium causes glycosuria.

W. D. H.

Action of Radium Emanations on the Respiratory Exchange. J. VON BENZGIGER and DIONYS FUCHS (*Chem. Zentr.*, 1913, i, 1444; from *Zeitsch. exp. Path. Ther.*, 1913, 12, 564—567).—Does;

even one hundred times greater than the ordinary therapeutic dose of radium emanation, have only a slight effect in increasing the gaseous exchange, and do not affect the combustion processes taking place in the organism. S. B. S.

Behaviour of Lecithin towards Radium Emanation and Thorium-X. CARL NEUBERG and LÁSZLÓ KARCZAG (*Chem. Zentr.*, 1913, i, 1356; from *Radium in Biol. Heilkunde*, 1913, 2, 116—122).—Different authors have assumed that the hæmolytic action of radium emanation and thorium-X is to be referred to a lecithin scission in the red corpuscles. It is found, however, that no hydrolysis takes place when solutions of the active substances are mixed with lecithin emulsions. The acidity does not rise, neither do the solutions differ in colour, odour, or consistence from the ordinary aqueous solutions. J. C. W.

Bürgi's Law of the Combined Action of Drugs. BÉLA VON ISSEKUTZ (*Pflüger's Archiv*, 1913, 151, 456—478. Compare A., 1912, ii, 667).—When two narcotics are introduced into the organism at the same time, or within a short interval, the combined effect is often greater than the sum of the effects of each individual drug. This increased effect is, according to Bürgi, greatest when the drugs have different cell receptors. This theory is adversely criticised in some detail by the author, who illustrates his arguments by numerous examples, both from his own experience and by quotations from the results of other workers. He draws the conclusion that it is difficult, if not impossible, to formulate any law which will explain the combined action of two drugs administered simultaneously. S. B. S.

Action of Adrenalin on the Respiration. DIONYS FUCHS and NIKOLAUS RÓTH (*Chem. Zentr.*, 1913, i, 1443; from *Zeitsch. exp. Path. Ther.*, 1913, 12, 568—571).—In experiments on men, similar results were obtained to those in the case of animals, namely, an increase in the volume in respiration. In man, however, there was no increase of frequency, as was observed in the case of animals. S. B. S.

Colchicine and its Derivatives. HERMANN FÜHNER (*Arch. exp. Path. Pharm.*, 1913, 72, 228—238).—The activity of some of Windaus's derivatives of colchicine was compared with that of the parent substance. Colchicine, in which only one of the enolic methoxy-groups of colchicine is saponified, is much less active than the methyl ether, colchicine. If the hydroxyl group is methylated, the original toxic value of colchicine is reached, or nearly so. Replacement of the acetyl group in this by benzoyl reduces the activity to one-tenth of that of colchicine. Oxycolchicine, obtained by oxidation with chromic acid, has on frogs an action resembling that of veratrine, but has no action when given to mammals. W. D. H.

The Influence of Cholesterol on Hæmolysis. G. JAHNSON-BLOHM (*Zeitsch. physiol. Chem.*, 1913, 85, 59—67).—The inhibitory

influence of cholesterol on the hæmolytic action of saponin, which was discovered by Ransom, was attributed by Windaus to the hydroxyl group of the former substance, and other views have been advanced to explain it. In the present experiments saponin and soaps were employed as hæmolytics, and the inhibiting action of cholesterol was confirmed; it is specially great if the temperature is raised, and increases with the time cholesterol is allowed to act. In saponin-hæmolysis an irreversible process between the red corpuscles and cholesterol occurs. In soap hæmolysis the action is less marked, and the explanation not so clear.

W. D. H.

The Influence of Cyanogen Gas on the Organism. JEAN LOUIS BURCKHARDT (*Arch. Hygiene*, 1913, 79, 1—24).—When cyanogen, in concentrations much below 0.1 mg. per litre of air, is inhaled by cats, it has no ill effects; in concentrations of 0.1 mg. per litre, it can be inhaled for half an hour without danger. When the concentration reaches 0.2 mg. per litre, it acts toxically within a few hours. Rabbits are less susceptible, and can tolerate concentrations of 0.4 mg. per litre; for these animals the toxic concentration lies between 0.6 and 0.8 mg. per litre. The symptoms are irritation of the mucous membrane, difficulty in respiration, and convulsions; death results from paralysis of the respiratory centre. The symptoms are apparently those of hydrogen cyanide poisoning, the cyanogen reacting in the organism according to the equation $(CN)_2 + 2KOH = KCN + KCNO + H_2O$. If this takes place, 1 mg. cyanogen must have the same toxic action as 1 mg. hydrocyanic acid; the latter is, however, according to Lehmann and his pupils, much more toxic. It is probable, therefore, that other secondary reactions take place. S. B. S.

The Physiological Action of Fraxin and its Behaviour in the Organism. GIOVANNI B. ZANDA (*Chem. Zentr.*, 1913, i, 1779; from *Arch. Pharmacol. experim.*, 1913, 15, 117—121).—Fraxin has small physiological action, and a dog can tolerate 2 grams per kilo. of body-weight without ill effects. It has no appreciable influence on blood-pressure or temperature, and the greater part is excreted unchanged within twenty-four hours. To the mouse, it is relatively non-toxic, but it shows a slight action on the activity of a frog's heart. S. B. S.

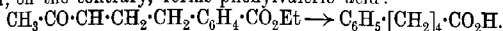
Anæmia Produced by the Hæmolysin from Streptococci. J. W. McLEOD and J. W. McNEE (*J. Path. Bact.*, 1913, 17, 534—537).—Rabbits vary in their susceptibility to streptolysin. Hæmoglobinæmia and hæmoglobinuria are produced, and the hæmolytic property of the filtrate is closely related to its toxicity. Incubation at 37° destroys toxic and hæmolytic properties. The bone marrow hypertrophies in long experiments, and changes were also noted in liver, kidneys, and spleen. Repeated injections produce increased susceptibility and no immunity. The hæmolysis *in vivo* is much less than *in vitro*. W. D. H.

Degradation of β Ketonic Acids in the Animal Organism.
 LEO HERMANN (Zeitsch. physiol. Chem., 1913, 85, 233—240).—It is uncertain whether, on decomposition of aliphatic acids in the organism, ketonic or acid intermediate compounds are formed. It is shown that ethyl phenylacetoacetate is decomposed into benzyl methyl ketone and hippuric acid. The ketone at first formed is converted into benzoic acid. When the ketone is administered to dogs, hippuric acid is recovered.

On subcutaneous injection of ethyl benzylacetoacetate, hippuric acid is formed in quantity, and only traces of phenylethyl methyl ketone. This ketone, when administered alone, yields exclusively phenaceturic acid. In this case, therefore, there is acid decomposition in contrast with the ketonic decomposition in the case of the phenyl ester.

Ethyl phenylpropylacetoacetate under similar conditions gives a good deal of hippuric acid, and traces of phenylbutyl methyl ketone.

When phenylbutyl methyl ketone is administered, only phenaceturic acid is obtained in the urine. The ketone is decomposed between the carbonyl and the methylene carbon, and phenylbutyric acid is formed: $C_6H_5 \cdot [CH_2]_4 \cdot CO \cdot CH_3 \rightarrow C_6H_5 \cdot [CH_2]_3 \cdot CO_2H$. The ester, on the contrary, forms phenylvaleric acid:



The phenyl group in ethyl phenylacetoacetate has thus an abnormal influence.

The normal formation of acetone in the body is due to similar secondary reactions. Normally, acetoacetic acid is degraded to acetic acid, but under pathological conditions the secondary reaction predominates and acetone is formed. The degradation of the fatty acids accordingly does not take place with the formation of ketones, but there is an elimination of two carbon atoms.

E. F. A.

The Influence of Salvarsan and Neosalvarsan on the Circulation and on the Kidneys of Healthy and Diseased Animals. ALWENS (Arch. expt. Path. Pharm., 1913, 72, 177—223).—Intravenous injection of salvarsan causes nephritis. Its toxicity increases not only with the dose given, but with the concentration; the histological appearances of the kidneys are described in detail; the nephritis is a vascular one, analogous to that produced by arsenic and cantharides. An immediate result of the injection, if made rapidly, is a fall in blood-pressure. Neosalvarsan produces clinically no nephritis, and in animals the nephritis produced by long-continued use of the drug is less marked; so also is the fall in blood-pressure. In animals which already have nephritis from other causes, the condition is intensified by very small doses of salvarsan, and in cases where the heart is diseased, the action of salvarsan on the circulation is most unfavourable. W. D. H.

The Relationship of Strophanthin Action and the Intensity of the Heart's Action. VIKTOR WEIZSÄCKER (Arch. expt. Path., 1913, 72, 282—294).—It was proved in experiments

on the frog's heart that the action of strophanthin takes place more rapidly the more quickly the heart is beating. In the resting heart, the drug is not completely inactive. The rate of beat being constant, rise of temperature increases the velocity of the action of strophanthin.

W. D. H.

The Resistance of Different Animals Towards Arsenic. M. WILLBERG (*Biochem. Zeitsch.*, 1913, 51, 231—252).—The following are the tolerated doses of potassium arsenite, expressed in mg. per kilo. of body-weight. For pigeons, less than 0.012 (subcutaneous); mice, 0.0156—0.0176 (subcutaneous); hedgehog, 0.01—0.014 (subcutaneous); rabbits, 0.008—0.01 (subcutaneous); dogs, 0.007 (subcutaneous or intravenous); guinea-pigs, 0.009 (subcutaneous); cats, 0.005—0.006 (subcutaneous); hares, more than 0.005 and less than 0.008 (subcutaneous); snakes, 0.012. The corresponding doses for arsenious acid are: For pigeons, 1.786 (per os); rabbits, 0.015 (per os); dogs, 0.03 (per os); hens, less than 0.06 (per os). It is noteworthy that the tolerance by man is less than by any of the above animals, which is probably due to the more highly developed nervous system. When arsenic is administered by the mouth, animals are to a large extent protected from the poisonous action by vomiting.

S. B. S.

Lipoids which Resemble Lecithin in Forming Hæmolysins along with Cobra-venom. JOHN CRUICKSHANK (*J. Path. Bact.*, 1913, 17, 619—622).—A number of substances were obtained from the alcoholic extracts of egg-yolk, heart, liver, and kidney, which differ from lecithin. They are all soluble in water, and with one exception in ether. They are precipitated from the ethereal solution by acetone. They all form hæmolysins along with cobra-venom.

W. D. H.

Action of the Lecithins on the Processes of Poisoning in Higher Animals. E. HANSCHMIDT (*Biochem. Zeitsch.*, 1913, 51, 171—192).—Lecithin by itself exerts no toxic action on animals, which can tolerate large doses, whatever method of administration is adopted. If injected together with curare, strychnine nitrate, ethyl alcohol, chloral hydrate, veronal, or morphine, it inhibited the action of these drugs. It increased, however, the toxic action of ricin. In the case of phosphorus poisoning, the effect of the lecithin appears to depend on the weight of the substance administered, smaller doses having apparently a beneficial, and larger doses a harmful, effect. The general condition of the animal and its body content in lipoids appears also to have some effect in this case.

S. B. S.

Poisoning by Methyl Alcohol. FRANCESCO OLIVARI (*Chim. Zentr.*, 1913, i, 1780; from *Arch. Farmacol. sperim.*, 1913, 15, 83—96).—The toxicity of crude and pure methyl alcohol for frogs, mice, and guinea-pigs was investigated. In the case of the pure products, the minimal lethal doses were: for frogs, $16.2^{\circ}/_{00}$; for

mice, 11.5⁰/₀₀; and for guinea-pigs, 9.5⁰/₀₀ of the body weight; the corresponding numbers for the crude acid product were 10.0, 7.5, and 6⁰/₀₀; and for the crude basic product, 8.6, 6.8, and 5.5⁰/₀₀. A scheme is given for the forensic examination of drinks, and animal organs in which wood-spirit is suspected. The liquid is acidified with phosphoric acid, and the volatile acids, etc., are distilled off, whilst the bases, pyridine, amines, etc., remain in the residue. The distillate containing the acids is neutralised, and again distilled, the salts of the acids remaining behind, the aldehydes, etc., distilling over. These are fixed by *m*-phenylenediamine hydrochloride, and the mixture is distilled, when acetone and methyl alcohol distil over, and are estimated in the distillate. If the mixture is saponified before these treatments, a conception can be formed as to the quantity of esters present from the amount of alcohol in this distillate. Finally, ethereal oils can be extracted by mineral oils (b. p. 140—230°), and separated from the higher alcohols by fractional distillation. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Formation of γ -Aminobutyric Acid from α -Glutamic Acid by Micro-organisms. EMIL ABDERHALDEN, GEORG FROMME and PAUL HIRSCH (*Zeitsch. physiol. Chem.*, 1913, 85, 131—135).—Whereas Ackermann (A., 1910, ii, 1089) identified γ -aminobutyric acid amongst the bacterial decomposition products of *d*-glutamic acid, Abderhalden and Kautzsch (A., 1912, i, 952) were unable to confirm this. It is now found that γ -aminobutyric acid is formed when a mixture of glutamic acid, dextrose, Witte's peptone, and inorganic salts is incubated with decomposing pancreatic tissue. Success depends on the presence of the proper micro-organism; the mixture contained various yeasts, together with Diplococci and Staphylococci. E. F. A.

Methods in Soil Bacteriology. VI. Ammonification in Soil and in Solution. FELIX LÖHNIS and HENRY HAMILTON GREEN (*Centr. Bakt. Par.*, 1913, ii, 37, 534—563).—A critical study of the factors affecting ammonification and nitrification of blood meal, flesh meal, and horn meal under laboratory conditions. Where the tests are carried out in solution and under aerobic conditions, the quantity of material does not appear to influence the rate of ammonification. Under anaerobic conditions there is a marked retardation of the process, due possibly to an accumulation of bacterial metabolic products. It is suggested that in the initial decomposition of flesh meal and horn meal in shallow layers of liquid, aerobic and anaerobic organisms play perhaps an equally

important part, but that aerobic organisms are concerned more actively with the later stages of ammonification. Under aerobic conditions, and with larger quantities of material, considerable amounts of ammonia may volatilise from the cultures, or undergo assimilation by bacteria. The decomposition of horn meal and blood meal is much more rapid in soil than in solution. When, however, soil tests in deep layers at full saturation are compared with solution tests in shallow layers, ammonification is faster in solution than in soil, and this would seem to indicate aeration as being one of the chief factors in determining the rate of decomposition in soils. The three materials used show differences among themselves in the rate of decomposition, and this varies again according as to whether the tests are made in solution or in soil. The conclusion is drawn that solution tests seem to afford more information concerning the nature of the materials used as sources of nitrogen.

Nitrification is not registered in solution in the presence of any of the materials, but in soil tests it keeps pace with ammonification provided that aeration is liberal, and that the quantity of ammonia formed is not excessive.

H. B. H.

The Oxidation of Thiosulphates on Bacterial Filters.
WILLIAM T. LOCKETT (*J. Soc. Chem. Ind.*, 1913, 32, 573—581).—

It has already been observed that phenol and thiocyanate undergo oxidation on bacterial filters (Fowler, Ardern, and Lockett, *A.*, 1911, ii, 139). In the present investigation, thiosulphate solutions were passed repeatedly through filters, consisting of stoneware pipes 24 in. long, cemented at one end and filled with clinkers. The amount of change in the solution was determined by an estimation of the oxygen absorbed from acid permanganate solution, and of the residual thiosulphate by $N/80$ -iodine. It was found that solutions up to 0.5% concentration (expressed as $Na_2S_2O_3$) can be oxidised; the resulting solution is acid, and the addition of alkali accelerates the rate of oxidation. The thiosulphate is oxidised finally to sulphate, but tetrathionate and pentathionate, with occasional traces of trithionate, are intermediately produced.

In an extension of the investigation to the thionic acids, it was first shown that the usual tests are applicable with but few exceptions to thionate solutions of 0.1 and 0.02% concentration. With the exception of the dithionates, all the thionates undergo oxidation in this manner; potassium trithionate is oxidised to sulphate with intermediate formation of a considerable quantity of tetrathionate; potassium tetrathionate gives sulphate with a little pentathionate, whilst potassium pentathionate is directly oxidised to sulphate.

The conclusion is drawn that the oxidation is due to bacterial agency assisted by the physical and chemical properties of the filtering medium.

D. F. T.

The Products of the Putrefaction of L-Aspartic Acid. New Method of Detecting β -Alanine. EMIL ABDEHOLDEN and ANDOR FODOR (*Zeitsch. physiol. Chem.*, 1913, 85, 112—130).—On putrefactive

decomposition of *L*-aspartic acid, succinic, propionic, and formic acids are formed (compare Neuberg and Cappezzuoli, A., 1909, ii, 691). These acids are easily separated by the ester method, as the acid esters may be extracted with ether from the ester hydrochlorides of the amino-acids.

Emphasis is laid on the necessity of carrying out putrefactive decomposition experiments with a single known organism or a mixture of known organisms. β -Alanine obtained by Ackermann (A., 1911, ii, 757) from aspartic acid could not now be identified. It is recognisable in the very smallest quantity by conversion into ethyl acrylate, which has a characteristic odour, and when added to a putrefaction experiment it is easily identified in this manner. Pure cultures of the five micro-organisms present were incubated separately with aspartic acid. In no case was β -alanine formed.

E. F. A.

Reaction Phases of Alcoholic Fermentation. HANS VON EULER and DAVID JOHANSSON (*Zeitsch. physiol. Chem.*, 1913, 85, 192—208).—It is shown generally that, when sugar is fermented in presence of phosphate, the relation between the amount of carbon dioxide liberated and the phosphate fixed throughout the whole course of the change is that expressed by Harden and Young's equation, namely, $2C_6H_{12}O_6 + 2PO_4HR_2 = 2CO_2 + 2C_2H_5O + 2H_2O + 2C_3H_{10}O_4(PO_4R_2)_2$. This expression by no means explains the mechanism of fermentation or the part played in it by the individual enzymes.

Fermentation begins with the conversion by means of an enzyme of the hexose sugars into a carbohydrate, which can be esterified with phosphate. The development of carbon dioxide which accompanies this esterification is checked by an excess of phosphate. The fermentation controlled by phosphate is accelerated by the presence of *l*-xylulose. Both hexose diphosphate and triosemonophosphate are formed. The enzymatic hydrolysis of the hexose phosphate ester studied by Harden and Young is materially retarded by the presence of toluene. All the foregoing facts must be taken into consideration in any explanation of the fermentative changes.

E. F. A.

Invertase Reaction of Mixed Yeast Cultures. ALBERT J. J. VANDELDE and A. VANDERSTRICT (*Biochem. Zeitsch.*, 1913, 51, 388—397).—The invertase action of mixed cultures lies generally between that of the varieties forming the mixture, which is in contrast to the effect observed with certain mixed cultures, on the alcoholic fermentation, where a mixture exerts a favouring action.

S. B. S.

Reduction of Acetaldehyde by Yeast Juice. S. KOSTYTSHEV and ELISE HÜBENET (*Zeitsch. physiol. Chem.*, 1913, 85, 408—411. Compare A., 1912, ii, 860).—An extract of dried yeast (maceration juice) is proved to reduce methylene-blue to the colourless state, and also acetaldehyde to alcohol, both in the presence and in the

absence of sugar. The active hydrogen in this case is probably formed in the same way as during zymase fermentation. E. F. A.

Are Moulds Able to Form Volatile Substances from Antimony Compounds? ERICH VON KNAFFL-LENZ (*Arch. exp. Path. Pharm.*, 1913, 72, 224—227).—The moulds investigated are not able to form volatile antimony compounds. In this there is a difference between antimony and the similar elements arsenic, selenium, and tellurium. The possibility that chronic antimony poisoning is due to the formation of volatile substances is excluded. W. D. H.

Nature of the Osmotic Optimum in Biological Processes. ALFRED GUILLEMARD (*Compt. rend.*, 1913, 156, 1552—1554).—A theoretical paper explaining results obtained in the culture of *Aspergillus niger* under various conditions. The living matter absorbs metallic compounds necessary for its physico-chemical constitution, the rate of formation of plant tissue following a curve which presents an optimum for a certain density with respect to the properties of the metal experimented with. The osmotic optimum occurs with most chemical substances in biological reactions. The amount of substance which favours it is the "excitation" dose, and precedes the "toxic" dose. W. G.

Replacement of Zinc by Copper in the Culture of *Aspergillus niger*. CHARLES LEPIERRE (*Compt. rend.*, 1913, 156, 1489—1491. Compare this vol., i, 326, 327).—Like cadmium, glucinum, and uranium, copper can replace zinc in the culture of *Aspergillus niger*. Added in the form of its sulphate, the weight of crop is normal if the amount of copper does not exceed 1 in 500,000, but the growth is retarded. If the amount rises to 1 in 1000, growth ceases. Sporulation takes place only if the copper present does not exceed 1 in 10,000. W. G.

The Assimilation of Guanine and Guanidine by Moulds. ALEXANDER KOSSOWITZ (*Chem. Zentr.*, 1913, i, 1297; from *Zeitsch. Gährungsphysiologie allg. landw. techn. Mykologie*, 1912, 2, 84—86).—Guanine could be used by a large number of moulds as a source both of carbon and nitrogen. These include *Botrytis bassiana*, *Penicillium glaucum*, *Mucor γ-Boidin*, *Cladosporium herbarum*, *Phytophthora infestans*, *Penicillium brevicaulis*, *Aspergillus glaucus* and *A. niger*, and *Isaria farinosa*. Guanidine, as carbonate, chloride, nitrate, or thiocyanate, could be used as a nitrogen source by all moulds. S. B. S.

Enzymatic Hydrolysis of Hippuric Acid by Mould Fungi. ARTHUR W. DOX and RAY E. NEIDIG (*Zeitsch. physiol. Chem.*, 1913, 85, 68—71. Compare A., 1909, i, 861; ii, 510).—Some characteristic mould fungi—three *Aspergillus* and three *Penicillium* species—were grown for periods of one, two, three, and four weeks in a nutrient solution consisting of sucrose, tartaric acid, and inorganic

salts. The mycelium was removed, ground with glass, the juice expressed, and its action on hippuric acid tested, the formation of glycine being detected by means of titration with formaldehyde. In most cases nearly complete hydrolysis was observed independently of the age of the culture. There is very little secondary action converting glycine into ammonia. Taka-diastase (made from *Aspergillus oryzae*) has a similar hydrolytic action on hippuric acid. E. F. A.

The Penetration of Different Forms of Nitrogen in Plants; Phenomena of Adsorption. D. CHOUCHAK (*Compt. rend.*, 1913, 156, 1696—1699. Compare Pouget and Chouchak, A., 1912, ii, 796, 975).—The roots of young wheat plants deprived of vitality by immersion in boiling water for thirty minutes retain the property of adsorbing and fixing nitrogen in different mineral and organic forms. This property is due to the presence of certain substances not removed by boiling water, but removed by boiling alcohol. This power of adsorbing different nitrogenous compounds, at the same molecular concentration, varies according to the nature of the compound, and for the same form of nitrogen, the amount of nitrogen adsorbed varies, within certain limits, directly with the concentration of the surrounding medium with respect to nitrogen. The ratio of the concentration of adsorbed nitrogen in the roots to that of the nitrogen remaining in the liquid is always greater than unity. W. G.

The Absorption of Different Forms of Nitrogen by the Plant; Influence of the Medium. D. CHOUCHAK (*Compt. rend.*, 1913, 156, 1784—1787. Compare preceding abstract).—The adsorbing power of the exterior layer of dead roots, and the rate of absorption or diffusion in the living plant, for the same concentration in nitrogen, is considerably modified by the presence of such salts as magnesium sulphate, sodium chloride, etc., and the effects produced by a number of these have been studied. They do not act in the same manner, but by their action on dead roots and on living plants they arrange themselves in the same order. In a mixture of two or more salts, they may help or be antagonistic to one another. In many cases the adsorption of nitrogen is very considerably increased, sodium chloride having a beneficial effect. W. G.

The Significance of Lipoids for the Formation of Bio-electrical Differences of Potential in Certain Plant Organs. JACQUES LOEB and REINHARD BRUTNER (*Biochem. Zeitsch.*, 1913, 51, 288—299).—The bio-electrical differences of potential already described by the authors at the undamaged surface of certain plant organs (apple, etc.) are qualitatively and quantitatively almost identical with that at the interface of an aqueous solution, and a solution of phosphatides in guaiacol, *m*-cresol, and amyl alcohol, and a guaiacol extract of apple behaves in this respect exactly like the undamaged organ itself. The solvents themselves without the

phosphatide have practically no action. Fatty acids which are insoluble in water, such as oleic and palmitic acids, show the same effect towards the varying concentrations of the aqueous salt solutions as the living organ. They behave, however, differently towards different concentrations of acids. The bio-electric action of the organs is not due therefore to fatty acids, neither is it due to cholesterol, the electromotor effects of which are quite different to those of the living organ. Solid proteins, such as coagulated egg-white or gelatin, also act in a different way. The bio-electric effects of the living organ are therefore ascribed to the presence of phosphatides or some similar insoluble substances. Cephalin and lecithin were used in the experiments in chains, which were constituted in the following way: $\text{Hg} \mid \text{HgClM} / \text{KCl} \mid \text{Guaiacol solution} \mid \text{KCl}$ in varying concentrations $\mid \text{M} / \text{KClHgCl} \mid \text{Hg}$.
S. B. S.

The Influence of Anæsthetics on the Potential Difference at the Surface of Living Animal and Vegetable Tissues. JACQUES LOEB and REINHARD BEUTNER (*Biochem. Zeitsch.*, 1913, 51, 300—306).—The addition of alcohol or ether to the aqueous phase diminishes the difference of potential at the interface of a living organ and an aqueous solution. The action is a reversible one. The quantities necessary to produce an effect are considerably larger than those necessary for the production of narcosis. A similar diminution of difference of potential is produced by the addition of alcohol or ether to the aqueous phase at the interface of an aqueous solution and a solution of oleic acid or lecithin in guaiacol. The action is due to the entrance of some ether into the non-aqueous phase. A similar action was not observed on the addition of an indifferent non-electrolyte, such as dextrose, to the aqueous phase.
S. B. S.

The Part Played by the Surface Tension and by Lipoids in the Living Cell. HORACE M. VERNON (*Biochem. Zeitsch.*, 1913, 51, 1—25).—Exosmosis of tannin from vegetable cells, caused by various narcotics, is apparently not a mere surface-tension phenomenon, as Czapek assumes. According to this observer, the substances cause exosmosis in those concentrations which reduce the surface tension of water/air to 0.685. Out of the twenty-nine substances investigated by Czapek, seven produce exosmosis in concentrations in which the surface tension varies between 0.82 and 0.998. The concentrations, according to the author, more nearly correspond with those which produce narcosis in tadpoles and hæmolysis of blood-corpuscles. The narcotics appear therefore to exert their action owing to their solubility in lipoids, according to the Overton theory. The part played by the lipoids in animal cells can be investigated by determining the concentration of the various substances which inhibit the action of indophenoloxidase, an insoluble ferment which only acts, according to the author, when the lipoids are intact. It is now found that the concentrations of narcotics which are just sufficient to inhibit this ferment action

are about twice as strong as those which cause exosmosis of tannin from *Echeveria* cells. The actual ratios vary between 0.9 and 2.8 for the seventeen substances investigated. As the concentrations varied between 1 and 720, the closeness of these ratios is striking. Colloidal sodium oleate acts in the same concentrations on *Echeveria* as on oxydase, whereas saponin acts on the oxydase in 1/40 of this concentration. Acids act on oxydase in concentrations corresponding more or less with the electrical conductivity of this solution, and there is a crude parallelism between these values and their hemolytic action.

S. B. S.

Carbohydrates of Vegetables. ERNST BUSOLT (*J. Landw.*, 1913, **61**, 153—160).—The sap of French beans (3000 c.c.), when kept for a week, yielded 9.3 grams of pure mannitol. No mannitol was found in the sap when quite fresh, or in sap which was at once sterilised by boiling and then kept for a week.

Cauliflower (1300 grams), without the stalk, yielded 7.9 grams of pure mannitol, which is supposed to have been present originally. It is, however, possible that the mannitol was produced during the evaporation of the sap.

N. H. J. M.

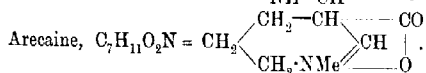
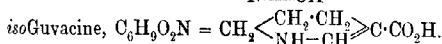
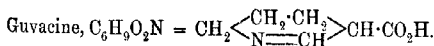
Simple Vegetable Bases. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1913, **85**, 372—391).—Emphasis is laid on the fact that the plant betaines are to be regarded as the simplest alkaloids formed from the amino-acids by exhaustive methylation.

The presence of glycine betaine and of choline in the alcoholic extract of oat seeds is established. In the phosphatide from oats, colamine (aminoethyl alcohol) but no betaine is present.

Glycine betaine may be identified as platinichloride. This salt undergoes a characteristic change when left in contact with its mother liquors.

Aminoethyl alcohol reacts quantitatively with nitrous acid, and may be estimated in this way. Since choline does not react with nitrous acid, the presence in it of 1% of colamine may be detected. Colamine is incompletely precipitated by phosphor-tungstic acid.

An investigation of the bases in areca nuts leads to the following formulæ being suggested:



These differ from the formulæ suggested by Jahns. E. F. A.

Formation of the Anthocyan Pigments of Plants. IV.
The Chromogens. FREDERICK KEFBLE, E. FRANKLAND ARMSTRONG, and W. NELSON JONES (*Proc. Roy. Soc.*, 1913, *B*, **86**, 308—317. Compare A., 1912, ii, 673; this vol., i, 325).—Flowers of any colour

variety of Brompton stocks, when treated with alcohol, lose their colour rapidly. The original colour is regained when the decolorised petals are placed in water, the recovery being rapid when the water is heated. The phenomenon is a general one, and it is also shown by the vegetative parts of plants. The brown wall-flower, which contains a mixture of purple anthocyan and yellow plastid colour, recovers purple. The power of recovering the original colour serves as a means of distinguishing anthocyan from plastid pigments. The recovery of the pigment is shown to be due to the oxidation of a chromogen.

The decolorisation is due to the activity of a reducing agent, which is extracted by alcohol. This is resistant to high temperatures, as the alcohol may be evaporated to dryness, and the residue taken up in water; it then contains an active reducing agent. This agent prevents the action of bran peroxylase on benzidine, whilst, when added to the blue solution resulting from the interaction of bran peroxylase, hydrogen peroxide, and benzidine, it brings about the decolorisation of the blue. Quinol has a similar effect, but not formaldehyde.

The flower petals contain a much larger quantity of chromogen than is used in the natural flower, as the colour may be removed and recovered several times. The amount of active water present in the cells determines the direction in which the pigment producing reaction shall go; as the amount of water decreases, the reducing agents become active and the oxydases inert.

The activity of α -glucose ceases in 60% ethyl alcohol and in 40% methyl alcohol. The activity of emulsin falls rapidly in alcohols up to 40% strength; in solutions with from 40 to 90% of alcohol the activity is proportional roughly to the amount of water present. Oxydase action ceases in about 70% alcohol, but in the plant cell the chromogens may undergo oxidation, even in 95% alcohol.

E. F. A.

Formation of the Anthocyan Pigments of Plants. V. Chromogens of White Flowers. W. NELSON JONES (*Proc. Roy. Soc.*, 1913, B, 86, 318—323. Compare Keeble and Armstrong, A., 1912, ii, 673).—Lack of colour in recessive white flowers may be the consequence, not of the absence of an essential constituent of the colour-producing mechanism, but of the failure of these constituents to come together and interact with one another. White flowers of *Lychnis coronaria* contain a chromogen which gives rise to a reddish-brown pigment on oxidation. The chromogen may be extracted by treatment with absolute alcohol; it reacts with the peroxylases in other plants in presence of hydrogen peroxide to form the brown pigment, and can thus be used in the same way as benzidine to demonstrate the distribution of oxydase. In *Lychnis* the natural conditions are never such as to allow any interaction between oxydase and chromogen. On treatment with alcohol or a similar hormone, the barrier is removed by the destruction of the plasmatic impermeability, and pigment is formed. The following types of white flowers have been demonstrated: (1) Those which contain

an oxydase and a chromogen, for example, *Lychnis coronaria*. (2) Those which contain a peroxydase and a chromogen, for example, *Dianthus*, sp. (3) Those which contain a peroxydase but no chromogen. These give no colour reaction after treatment with chloroform and hydrogen peroxide. (4) Those which contain no peroxydase.

E. F. A.

Variation in the Composition of Water-Trefoil (*Menyanthes trifoliata*, L.) during a Season's Growth. MARC BRIDEL (*J. Pharm. Chm.*, 1913, [vii], 7, 529—535. Compare A., 1911, i, 559).—This investigation was carried out on the same lines as were adopted in the case of gentian root (A., 1911, ii, 426), with the exceptions that (1) the carbohydrates hydrolysed by invertase in the water-trefoil are unknown, and (2) that meliatin, unlike gentiopicroin, cannot be isolated and weighed. The proportion of meliatin was therefore estimated by the change in rotation induced by emulsin in an aqueous solution of a dry alcoholic extract of the plant, in which (1) the initial reducing sugar, and (2) the carbohydrates hydrolysed by invertase had already been determined.

The results, tabulated in the original, show that the plant contains most meliatin (0.891%) towards the end of May, and least (0.655%) at the beginning of October. The carbohydrates hydrolysed by invertase are at a minimum (0.950%) at the middle of June, and increase steadily to 2.761% at the beginning of October. As in the case of gentian, it appears that the percentage of glucoside shows little variation, so that this substance cannot be regarded as a reserve material. On the other hand, the carbohydrates are accumulated as reserve materials up to the period at which the fruit ripens, to be used at the resumption of vegetative activity.

T. A. H.

Husks of Buckwheat Seeds. KURT FESSLER (*Zeitsch. physiol. Chem.*, 1913, 85, 148—155).—The brown husks of buckwheat seeds are reputed to contain a green pigment not identical with chlorophyll. The poisonous action of the husks towards animals is attributed to the photodynamic action of this pigment. The green pigment has now been studied more in detail and its absorption spectrum recorded; it shows red or brownish-red fluorescence in organic solvents. On keeping, the green colour changes to a yellow or brownish-green.

A yellow xanthophyll pigment is also present, which is closely related to phytosterol. The brown pigment of the husks is identified as a phlobaphen.

E. F. A.

The Fruit of *Crataegus macracantha*. W. BRUCE ARMSTRONG (*Chem. News*, 1913, [iv], 13, 280—281).—The fruits yielded 17.98% of sugars, 2.085% of ash, and contained 0.595% of nitrogen and 0.79% of oil. Protein was detected in all the fruits, and Wagner's reagent and the phenolphthalein test indicated that atropine may be present, although no other evidence of this could be obtained.

The ash had the following percentage composition: Al_2O_3 (trace of iron), 6.86; CaO , 13.93; MgO , 12.16; K_2O , 23.80; Na_2O , 37.63; SO_3 , 3.09; Mn , 0.10; Cl , 0.15. The sugars present included dextrose and levulose. Acetic and citric acids were also present, the former due to fermentation. T. A. H.

The Pharmacognosy of the Manna Ash. GIOVANNI B. ZANDA (*Chem. Zentr.*, 1913, i, 1779; from *Arch. Farmacol. speriment.*, 1913, 15, 66—82).—Details are given for the preparation of the manna. To separate mannitol from fraxin, the aqueous extract of *Fraxinus* bark is treated with neutral lead acetate, the mixture is filtered, and then basic lead acetate is added. The mannitol in the filtrate can be estimated gravimetrically or polarimetrically. The fraxin is precipitated as a lead compound, which is decomposed by hydrogen sulphide. The product thus obtained is freed from tannic acid by treatment with a small quantity of water and recrystallised from alcohol. The fraxin can be estimated by titration with Fehling's solution after hydrolysis with dilute hydrochloric acid. The mannitol and fraxin contents of various species and of trees from different provinces and in different seasons were also investigated. When the quantity of mannitol is relatively large, that of fraxin is small and vice versa. S. B. S.

Presence of Gentiopicroin in the Leaf-bearing Stems of Gentiana spp. MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], 7, 486—492. Compare this vol., i, 434).—The leaf-bearing stems of *Gentiana cruciata*, L., *G. lutea*, L., and *G. asclepiadea*, L., were first examined by Bourquelot's biochemical method, and gave indications of the presence of gentiopicroin. The latter was then extracted from each of these materials. The first-named plant yielded very little, in which respect it resembles *G. pneumonanthe*, the stems of which also contain only a small amount of the glucoside (A., 1910, ii, 887). T. A. H.

Fruit of American Holly (*Ilex opaca*). F. F. CARHART and G. H. MILLER (*Chem. News*, 1913, 107, 243—244).—The dry fruit contained 46.34% of reducing sugars, 8.31% of ash, 0.61% of nitrogen, and 1.5% of oil, as well as oxalic acid and proteins. The reducing sugars include dextrose and levulose. The percentages of the constituents of the ash are as follows: SO_3 , 4.59; Al_2O_3 , 10.08; Fe_2O_3 , 1.27; CaO , 15.91; MgO , 8.01; P_2O_5 , 14.06; K_2O , 17.15; Na_2O , 24.32; MnO , 0.10; Cr , nil. The oil had D 0.9358 and saponification equivalent 303, and appeared to belong to the castor oil group. T. A. H.

Comparison of the Hydrolysing Diastases of the Latex of *Maclura aurantiaca* with those of *Ficus carica* and *Broussonetia papyrifera*. C. GERBER (*Compt. rend.*, 1913, 156, 1573—1575).—The latex of *Maclura aurantiaca*, like those of *Broussonetia papyrifera* and *Ficus carica*, merits the name of "vegetable pancreatic juice." Like them, and in the same way as

animal pancreatic juice, it hydrolyses and renders soluble carbohydrates, fat and protein substances, and plays a primary part in the nutrition of the plant. These properties are due to the existence of certain enzymes, the characteristics of which are intermediate between those of the enzymes of the *Broussonetia* and *Ficus*, and place the latex of the *Maclura aurantiaca* between those of these two plants, and nearer to the first than the second.

W. G.

Migration of the Constituents of Maize Grain in Water and Aqueous Solutions. EDMOND POPPE (*Bull. Soc. chim. Belg.*, 1913, 27, 103—109. Compare A., 1911, ii, 428).—Maize grains, when steeped in water or in dilute aqueous solutions of chlorides, nitrates, phosphates, or sulphates, or in saturated solutions of sucrose or sodium chloride, at the ordinary temperature for forty-eight hours, lose but very small amounts of their constituents. If, however, they are steeped in boiling solutions, a large amount of the nutritive substances is removed, and the grains diminish in alimentary value by 36.2%. Dilute solutions of the above-mentioned salts behave as distilled water with respect to the amount of nutrients removed. The ordinary temperature is not sufficiently high to kill the epidermic cells and so destroy their semi-permeability, but this occurs at the higher temperature, and the cell-walls become permeable to all the substances dissolved in the water. W. G.

Some Data on the Ripening of Florida Oranges. F. ALEX. McDERMOTT (*J. Amer. Chem. Soc.*, 1913, 35, 834—837).—A study has been made of the enzymes in the peel of Florida oranges with a view to ascertaining whether any change takes place in their nature or activity at the point at which the fruit becomes sufficiently ripe for consumption. The peel contains peroxydase, catalase, and invertase enzymes, but no oxydases. During ripening, the weight of the peel decreases in relation to the total weight, whilst that of the juice increases about equally in this relation. The total amount of acid in the juice decreases only slightly, but its concentration decreases considerably, whilst the sugar increases both in concentration and total amount. E. G.

Chemical Examination of the Roots of Phaseolus multiflorus, Lam. FREDERICK B. POWER and ARTHUR H. SALWAY (*Pharm. J.*, 1913, [iv], 36, 550—552).—The statement having been made that the roots of this plant (scarlet runner bean) are poisonous, the authors have submitted the roots to a systematic chemical examination, and have isolated a number of definite constituents. Physiological tests of certain of these constituents, and of extracts of the roots, furnished no evidence that the roots are toxic.

An aqueous extract of the roots on precipitation with alcohol furnished a preparation which hydrolysed amygdalin and gave the biuret reaction. No hydrocyanic acid was formed on macerating the ground roots in water.

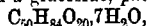
An alcoholic extract of the roots was mixed with water and

steam distilled, and thus separated into (a) a small amount of brown essential oil, (b) resinous matter, and (c) matter soluble in water. From the last-mentioned portion furan-3-carboxylic acid (compare Rogerson, T., 1912, 101, 1044), allantoin (compare Ackroyd, A., 1911, ii, 308; Titherley and Coppin, A., 1912, ii, 289), an amorphous, glucosidic substance, and a reducing sugar which furnished *d*-phenylglucosazone were obtained.

The resinous matter was extracted successively with light petroleum, ether, chloroform, ethyl acetate, and alcohol. The material soluble in light petroleum was heated with alcoholic potassium hydroxide, and from the product of this reaction a *phytosterol*, $C_{27}H_{46}O$, m. p. 130° , pentatriacontane, and a *phytosterolin*, m. p. 275° (acetyl derivative, m. p. 162°), were isolated, as well as a mixture of solid fatty acids, which had m. p. 55° , and some liquid fatty acids, consisting of oleic, linoleic, and a third acid of lower molecular weight.

From the ether, ethyl acetate, and chloroform extracts nothing definite was isolated, but the second contained some glucosidic material.

The portion insoluble in the foregoing organic solvents, but soluble in alcohol, yielded a glucoside, *phaseosaponin*,



m. p. 238° (decomp.), crystallising in colourless leaflets, and having the properties of a saponin. On hydrolysis by hot dilute hydrochloric acid, this furnished rhamnose (4 mols.) and *phaseosapogenin*, $C_{36}H_{44}O$, m. p. 200° (dry, decomp.), which could not be obtained crystalline. A different saponin and sapogenin of the above empirical composition were found by van der Haar in *Polyscias nodosa*, Forst (A., 1912, i, 885). T. A. H.

Pine Nut Oil. MAXWELL ADAMS and AUGUST HOLMES (*J. Ind. Eng. Chem.*, 1913, 5, 285—287).—The seeds obtained from the cones of the nut pine (*Pinus Monophylla* or *P. Fremontiana*), a tree growing on the Sierra Nevada Mountains, California, yield about 12% of oil having an aromatic odour and agreeable taste; it is light yellow in colour, but becomes colourless on exposure to light. The oil has m. p. -15° , b. p. $305^{\circ}/60$ mm., n_D^{20} 1.4543, saponification number 189.3, iodine number (Hübl) 108, and consists chiefly of olein, together with small quantities of stearin, palmitin, laurin, and linolein. W. P. S.

Fruit of the "Snowberry" (*Symphocarpus racemosus*). C. B. SMITH (*Chem. News*, 1913, 107, 266).—The dried fruits contained 4.1% ash, 17.17% sugars, 1.1% of oil, 0.59% nitrogen (=3.68% protein) as well as tartaric and citric acids and a trace of malic acid. No alkaloids were found. The ash had the following percentage composition: SiO_2 , 0.78; Fe_2O_3 , 2.10; Al_2O_3 , 3.15; CaO , 15.11; MgO , 6.30; Na_2O , 8.32; K_2O , 40.26; SO_3 , 6.95; P_2O_5 , 14.87; Mn, 0.94. The sugars probably included dextrose and laevulose. The oil had saponification value 212.3. T. A. H.

Imbibition of Strychnos Seed. EDUARD VERSCHAFFELT (*Pharm. Weekblad*, 1913, 50, 697—706).—The seed of *Strychnos Nux vomica* has a cuticular layer permeated very slowly by water. The presence of this layer greatly retards the imbibition of the seed, but addition of chloroform, ethyl acetate, and certain other organic substances produces a marked augmentation in the permeability to water, and hence in the velocity of imbibition. A. J. W.

Occurrence of Barium in Tobacco and Other Plants. JAMES S. MCHARGUE (*J. Amer. Chem. Soc.*, 1913, 35, 826—834).—Crawford (*Bull.* No. 129, *Bur. Plant Indust., U.S. Dept. Agric.*) has shown that the poisonous effect of loco-weed (*Astragalus* spp.) on cattle is due to the presence of barium, and further work has shown that barium is of common occurrence in plant tissues and soils.

Barium has now been found in tobacco in amounts varying from 0.009% to 0.074% (calculated as BaSO_4). Some of the barium can be extracted from the leaves by means of water, and is probably present in combination with organic acids. It is suggested that the occurrence of barium in living cells of the higher plants may indicate that the metal has some metabolic function. E. G.

Constituents of the Leaves of *Zygadenus intermedius*. III. FREDERICK W. HEYL and F. E. HEPNER (*J. Amer. Chem. Soc.*, 1913, 35, 803—811).—In an earlier paper (this vol., i, 386) an account has been given of zygadenine, a crystalline alkaloid obtained from the leaves of *Zygadenus intermedius*. Further investigation of the leaves has shown that in addition to the alkaloid, sucrose, reducing sugars, and dextrin (A., 1911, ii, 326), they also contain the following substances: Quercetin; cerotic acid; a *phytosterol*, m. p. 135°, $[\alpha]_D^{25}$ —29.5°, which yields an *acetyl* derivative, m. p. 122—123°; hentriacontane, m. p. 68°; a fat, composed of the glycerides of stearic, palmitic, linolic, oleic, and isolinolenic acids; a polyhydric *alcohol*, m. p. 285—288°, of the ipuranol class; and a crystalline substance, m. p. 112—114°, which has not been identified.

The ash from (1) the leaves and tops and (2) the bulbs had the following composition, the first figure in each case referring to (1) and the second to (2): Moisture, 3.79, 2.04; Cl, 0.30, 0.19; CO_2 , 18.05, 16.61; sand, 8.31, 7.01; C, 0.71, 0.48; soluble SiO_2 , 4.39, 3.55; SO_3 , 2.89, 3.33; P_2O_5 , 5.03, 8.73; Fe_2O_3 , 1.03, 1.08; Al_2O_3 , 2.55, 1.08; Mn, traces; CaO, 25.37, 26.48; MgO, 5.34, 5.02; Na_2O , 5.58, 4.68; K_2O , 20.64, 20.35. E. G.

Acidity in Silage: Method of Estimation. C. O. SWANSON, J. W. CALVIN, and EDWIN HUNGERFORD (*J. Amer. Chem. Soc.*, 1913, 35, 476—483).—The estimation of acidity in silage is usually carried out on an aqueous extract (compare Hart and Willaman, A., 1912, ii, 1205; Dox and Neidig, this vol., i, 236). A comparison has now been made of the efficiency of water and alcohol as extracting agents, and it has been found that equally uniform results are obtained by means of either solvent, but that the alcoholic extracts always contain a higher percentage of acids than the aqueous. It

therefore follows that some of the acids in silage are soluble in alcohol, but insoluble in water. The quantities insoluble in water vary with different kinds of silage, but are greatest in maize silage.
E. G.

Occurrence of Methyl Alcohol in Fruit Wides. HUGO BAUER and R. ENGLER (*Pharm. Zentr.-h.*, 1913, 54, 445—447. Compare Wolff, A., 1901, i, 110).—Methyl alcohol was found in currant wine; the amount was too small to be of practical importance.

N. H. J. M.

The Part Played by Oxydases in the Curly Top Disease of Sugar Beet. HERBERT H. BUNZEL (*Biochem. Zeitsch.*, 1913, 50, 185—208).—Leaves of plants with this disease contain two to three times as much oxydase as those of normal plants. No differences could be detected in the roots. In beets in which the growth was impeded by other factors, no abnormally high content in oxydase could be detected. The difference in the oxydase content of leaves of different plants is not merely a function of their size, and young and healthy leaves are normal in this respect. Where a normal function of the plants is suppressed, such as the formation of seeds, there is a high oxydase content. The general conclusion is drawn that abnormal disturbances of growth lead to an increased oxydase content of the leaves. Attention is called to similar high oxydase contents in other plant diseases. The general distribution of the oxydases in the various juices of the plant was also investigated. The expressed juice of seeds is richest in oxydase; then follow the leaves and roots.

S. B. S.

Action of Flowers of Sulphur on the Growth of Sugar Beet. JOSEF URBAN (*Zeitsch. Zuckerind. Böhm.*, 1913, 37, 441—444).—Application of flowers of sulphur slightly increased the yield of sugar beet. The sulphur was without effect on the colour of the leaves, and also had no effect on the amount of sugar and the quality of the juice.

N. H. J. M.

The Acids in Honey. ALFRED HEIDUSCHKA and G. KAUFMANN (*Chem. Zentr.*, 1913, i, 1221; from *Südd. Apoth.-Zeit.*, 1913, 53, 118—119).—About half of the volatile acids in honey is represented by formic acid, which was estimated in the steam-distillate and found to compose 0.0037 to 0.0072% of the substance. The non-volatile acids were estimated by the method of Heiduschka and Quincke (*A.*, 1908, ii, 73) with the result: Lactic acid, 0.0225%; malic acid, 0.0019%; traces of tartaric acid; the merest traces of higher fatty or wax acids; no succinic acid; phosphoric acid, 0.0286% as P_2O_5 . This accounts for about one-quarter of the total acidity as measured by 0.1N-potassium hydroxide. The remainder is largely due to carbon dioxide and to amphoteric substances.

J. C. W.

Behaviour of Nitrates in Soils. IGNAZ VOGEL (*Landw. Versuchs-Stat.*, 1913, 82, 158—159. Compare A., 1912, ii, 1206).—The high

and irregular losses of nitrogen previously observed are now shown to be due to absorption of nitrates by the glazed dishes in which the soils were kept. Subsequent experiments showed, however, that light humous soils, kept in thin layers, may lose, in a few days, 10–12% of the nitrates present. The loss of nitrates is now attributed to denitrification, and not to a chemical decomposition of nitrates, or to assimilation.

N. H. J. M.

The Behaviour of Acid Amides in the Soil. SAMUEL L. JOBIDI (*J. Franklin Inst.*, 1913, 175, 245–258. Compare A., 1910, ii, 339; 1911, ii, 820).—The author, having previously shown the different forms in which organic nitrogen exists in soils, now describes experiments on the ammonification of acetamide and propionamide when mixed with soil under different conditions; after varying intervals of time these mixtures were distilled with either magnesium oxide or barium carbonate, and the evolved ammonia carefully estimated.

It is found that acetamide and propionamide readily undergo ammonification when mixed with soil, that the rate of transformation is greatly influenced by the chemical structure of the amide, and that the maximum percentage of ammonia obtained from acetamide and propionamide is 83.43% and 75.14% respectively.

F. M. G. M.

Fixation of Ammonia by Permutite and Clay Soils. Availability of Permutite Nitrogen for Plants. DAVID J. HISSINK (*Landw. Versuchs-Stat.*, 1913, 81, 377–432).—The results of pot experiments showed that oats assimilate nitrogen as ammonium sulphate and as permutite nitrogen about equally well, 70% of both being utilised. The solubility of the two forms of nitrogen in water saturated with carbon dioxide is, however, totally different, permutite nitrogen requiring 1300 to 1400 times as much water as the nitrogen of ammonium sulphate held by a clay soil.

The very slow liberation of ammonia from permutite indicates that the ammonia is partly chemically combined, and not merely held by adsorption.

N. H. J. M.

Evolution of Sulphur in Soil; Study of its Oxidation. CH. BIAUX and MARCEL GUERRET (*Compt. rend.*, 1913, 156, 1476–1479).—A study of the oxidation of sulphur when introduced into various kinds of soil, with or without the addition of certain other substances. The results show that the oxidation is almost entirely due to microbic action. With garden soil the oxidation is slow at first, but becomes very rapid after the tenth day, the introduction of carbohydrates, such as sucrose and starch, having a marked retarding influence on the rate of oxidation, whilst peptone produces very considerable increase in the oxidation after the fifteenth day. The addition of chalk to a soil poor in lime increases the rate of oxidation by fixing the sulphuric acid formed. The inoculation of sterilised soil by ordinary soil water increases the rate of oxidation by about twenty to sixty times.

W. G.

Chemical Causes and Character of the Injurious Effect of Large Amounts of Lime on Peat Soil. GEORG A. RITTER (*Bied. Zentr.*, 1913, 42, 239—242; from *Fühling's Landw. Zeit.*, 1912, 593).—The losses of nitrogen which take place when lime and nitrates are applied to peat are attributed to chemical and not to biological action. A very small part of the loss may be due to the production of nitro-compounds from humus; the main cause of the destruction of nitrates is the reducing action of the humus.

The injury to vegetation observed when lime alone is applied in large amounts to peat cannot be due to the destruction of nitrates, since no nitrates are present, but to the increased oxidation of the organic matter and the production of substances, such as oxalic, formic, and acetic acids, etc., which are injurious to plants.

N. H. J. M.

Influence of Humus on the Weathering of Silicates. H. NIKLAS (*Bied. Zentr.*, 1913, 42, 231—232; from *Intern. Min. Bodenk.*, 1912, 2, 214).—The results of experiments in which silicates were kept in contact with peat for seven years, showed that the silicates were only very slightly attacked.

N. H. J. M.

Zeolitic Properties of Ground Phonolite and Lime Trass Manure Compared with some Soil Varieties. ERICH BUSSMANN (*J. Landw.*, 1913, 61, 97—134).—The ammonia of ammonium chloride is very strongly and chemically absorbed by lime trass; it is strongly absorbed by marsh soil, and well absorbed by phonolite, whilst red soils and loam have respectively only moderate and slight absorptive properties. All the substances adsorb potassium in dilute solutions, and absorb it in strong solutions. Calcium is only notably absorbed by lime trass. Nitrogen as nitrates is not absorbed by any of the substances, and magnesium only by lime trass and marsh soil. Phosphoric acid is fixed chemically, most by lime trass, and least by lime.

Under certain conditions the addition of phonolite and lime trass is favourable to the activity of *Azotobacter*, and consequently induce increased fixation of nitrogen in the soil. The sum of factors which produce this result is, however, still unknown.

N. H. J. M.

Manure Analyses. EILHARD ALFRED MITSCHERLICH, and WILH. SIMMERMACHER (*Landw. Jahrb.*, 1912, 43, 405—435).—A continuation of the author's work on the law of minimum as a logarithmic function (compare A., 1911, ii, 760). Numerous analyses are described, and the results tabulated, from which the author deduces formulæ supporting his theory. F. M. G. M.

Organic Chemistry.

Formation of Pure Methane from Aluminium Carbide. ENRIQUE HAUSER (*Anal. Fis. Quim.*, 1913, 11, 317—319).—The carbide may on treatment with water yield alkali hydroxides, which with metallic aluminium give hydrogen, which in one case amounted to 8% of the gas. G. D. L.

The Inflammability of Acetylene Mixed with Approximately 30% of Air. MARCEL DELEPINE (*Eighth Inter. Cong. App. Chem.*, 1912, 4, 25—28).—In a series of experiments on the inflammability of mixtures of acetylene and air in approximately the proportion 70 : 30, an ovoid globe of one litre capacity was used. Electric sparks 2 mm. in length failed to ignite the gas even when the pressure was increased to $1\frac{1}{2}$ atmospheres. An electrically heated platinum wire is more effective than one of iron, for a wire of the latter metal, 2 cm. in length, caused ignition only when the additional pressure was 3.5 cm. and the wire was actually fused. The effect of the extent of the heated surface is indicated by the failure of a platinum wire 10 mm. long and 0.1 mm. in diameter to inflame a mixture under 11.3 cm. additional pressure although the wire fused, whilst a wire 0.2 mm. in diameter and 20—30 mm. long inflamed the gaseous mixture even when the pressure was slightly reduced; the latter wire failed to ignite a similar gaseous mixture enclosed in a lead tube 20 mm. in diameter and 1.4 mm. long. Mercury fulminate is very active in causing ignition, for although 0.005 gram failed to affect a mixture containing 29% of air, 0.01 gram caused inflammation in a mixture containing 28% of air under an additional pressure of 1 cm.; if the air is reduced to 23%, however, the pressure must be increased by more than 9 cms. before ignition is caused by this quantity of fulminate.

The initiation of the combustion is believed to be due to the primary decomposition of the acetylene giving hydrogen which forms a more combustible mixture with the air; the combustion of the new mixture then induces the inflammation of the remaining gas. It is suggested that the decrease in inflammability in the lead tube used above is due to the rapid mixing of the hydrogen and air being checked. D. F. T.

Action of Acetylene on Some Copper Compounds: New Cupro-Acetylene Compounds. FELIPE LAVILLA LORENS (*Anal. Fis. Quim.*, 1913, 11, 320—327).—When pure acetylene is allowed to act on a 10% solution of copper sulphate, to which is added 3 volumes of a 20% solution of sodium sulphite, there is first precipitated the compound $\text{Cu}_2\text{SO}_3 \cdot \text{Cu}_2\text{C}_2$ of a clear red colour. When an excess of acetylene is employed, the dark red $\text{Cu}_2\text{SO}_3 \cdot 2\text{Cu}_2\text{C}_2$ is formed. When acetylene in excess acts for a long period on the well washed precipitates obtained from copper sulphate by means of sodium hydroxide or carbonate, or ammonium hydroxide, a black, explosive substance of the composition $\text{C}_6\text{Cu}_3 \cdot \text{H}_2\text{O}$ is obtained. G. D. L.

Action of Alkali Hydroxide and of Dry Silver Oxide on Trimethylene Bromide. B. F. FORTINSKI (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 568—580).—The author reviews the literature dealing with the formation of β -oxides, and describes attempts to prepare such an oxide from α -dibromopropane.

The action of aqueous potassium hydroxide on α -dibromopropane yields allyl alcohol and β -propylene glycol; the latter forms a *phenylurethane*, $C_{17}H_{18}O_4N_2$, m. p. 137—137.5°.

The reaction occurring between dry silver oxide and α -dibromopropane is very energetic, but in presence of ether proceeds more smoothly, the products being β -propylene glycol and a compound of high boiling point which is converted into the same glycol by treatment with 10% sulphuric acid solution, and is hence probably a double β -oxide.

T. H. P.

Oxidation of Alcohols under the Influence of Heat. JEAN B. SENDERENS (*Compt. rend.*, 1913, 156, 1909—1912).—As a preliminary to the investigation of the oxidation of alcohols in presence of various metals and metallic oxides, the action of hot air on various alcohols has been examined, and it is shown that oxidation occurs at lower temperatures than has previously been supposed.

The experiments were made by passing a mixture of dry air and the vapour of the alcohol into a vacuum glass tube, heated to the required temperature. The air was passed in at the rate of 100 c.c. per minute. Under these conditions, the oxidation of ethyl alcohol begins at 405°, and the issuing gas contains no oxygen, when the temperature is raised to 450°. The corresponding temperatures for isobutyl alcohol are 400° and 435°, and for isoamyl alcohol, 380° and 410°. The principal product is carbon monoxide, but some dioxide is also formed, and at the lower temperatures some aldehyde and acid are produced. In the case of ethyl alcohol the issuing gas contains also some ethylene, methane, and hydrogen. Magnesium turnings, finely-granulated zinc, aluminium powder, molybdic anhydride, blue tungstic oxide, thorium and silica only feebly assist or accelerate these reactions, whereas vanadic anhydride lowers the temperature at which oxidation begins, and accelerates the absorption of oxygen, and is therefore a true catalyst (compare Naumann, Moeser and Lindenbaum, A., 1907, ii, 273).

T. A. H.

The Hydrogenation of Some Secondary *l*-Ethylenic Alcohols in the Presence of Nickel. ROGER DOUKIS (*Compt. rend.*, 1913, 157, 55—57).—By the passage of secondary ethylenic alcohols of the type $CHR:CHR'OH$ over reduced nickel at 200°, they are converted, by isomerisation, into the corresponding ketones, $CH_2R \cdot CH_2COH$, some of the saturated hydrocarbon $CH_2R \cdot CH_2 \cdot CH_2R'$ being formed at the same time. The secondary ethylenic alcohols are readily obtained by the condensation of magnesium alkyl haloids with acetaldehyde or crotonaldehyde (compare Grignard, A., 1901, i, 679). Thus isoamyl-propenylcarbinol is converted into *propyl isoamyl ketone*, $C_9H_{18}CO$, b. p. 177—179°, D_4^{20} 0.8362, D_4^{25} 0.8205, giving a *semicarbazone*, m. p. 107°. This ketone is also obtained by oxidation of *propylisoamyl*

Any change tending to remove water should therefore cause a lightening of the colour. This is confirmed. The deeply coloured cold 1.5% solution of vanadium pentoxide in ethyl alcohol becomes colourless at 60–70°, but if diluted with an equal volume of absolute alcohol the change takes place at 50–60°, whilst the addition of a few drops of water raises the temperature of the change to above 70°. Anhydrous copper sulphate removes most of the colour at the ordinary temperature. An excess of alcohol in the cold does not alter the colour, but only affects the temperature at which the change takes place. The electrical conductivity diminishes at the same time as the colour, and only begins to increase with the temperature after decolorisation is complete. The conductivity also diminishes with increasing concentration of the alcohol. Pure ethyl orthovanadate has a very small conductivity. A solution of 1 mol. V_2O_5 in 1.09 mol. Na_2O exhibits similar colour changes to the ester.

The esters, especially *tert.*butyl orthovanadate, are very suitable for the preparation of clear colloidal solutions of vanadic acid, as the alcohol is easily removed by boiling.

Ethyl orthovanadate, Et_3VO_4 , is a bright yellow liquid, b. p. 98.5°/16 mm., and 152°/145 mm., D^{15}_4 1.167, forming white crystals in liquid air. A greenish-black, crystalline compound, $V_4C_{16}H_{40}O_{18}$, is obtained by heating the ester at 160–170°, acetaldehyde and ether being evolved. Propyl orthovanadate, Pr_3VO_4 , has b. p. 143°/24 mm., D^{15}_4 1.088, and forms an amber-coloured glass in liquid air. *n*-Butyl orthovanadate, $(C_4H_9)_3VO_4$, has b. p. 175°/22 mm., and the *iso*-propyl ester, b. p. 149°/16 mm., and D^{15}_4 1.033.

*tert.*Butyl orthovanadate, b. p. 117°/15 mm., forms colourless crystals, m. p. 45–47°. *iso*-Amyl orthovanadate forms yellow crystals, m. p. about 70°, b. p. 185–187°/18 mm. The *tert.*amyl ester, $(C_5H_{11})_3VO_4$, is a colourless liquid, b. p. 161°/19 mm., D^{15}_4 0.993, and is stable towards air and water.

Ethyl trivanadate (*metavanadate*), $Et_3V_3O_9$, is a light yellow powder, which readily decomposes. The molecular weight determination in phenol gives figures corresponding with the above formula. The *n*-propyl and *iso*-amyl esters have similar properties.

Vanadium oxychloride and sodium ethoxide react in benzene, forming *diethyl chloro orthovanadate*, $VOCl(OEt)_2$, a dark red liquid, b. p. 103°/33 mm., D^{15}_4 1.366. By using suitable proportions, *ethyl dichloro orthovanadate*, $VOCl_2 \cdot OEt$, is obtained as a red liquid, b. p. 103°/49.5 mm.

The methyl esters have not been isolated, and glycerol and benzyl alcohol are oxidised by vanadium pentoxide.

Aniline hexavanadate, $(NH_3Ph)_4V_6O_{17} \cdot 2H_2O$, forms reddish-brown monoclinic prisms, $a:b:c = 0.4912:1:0.8511$, β 93°57'. Vanadium oxychloride forms an *additive product*, $VOCl_2 \cdot 2Et_2O \cdot 2H_2O$.

C. H. D.

The Methods for the Synthesis of Glycerides. ADOLF GRUBER (*Ber.*, 1913, 46, 2198–2200).—Polemical. A criticism of the results and conclusions of van Eldik Thieme (this vol., i, 701). J. C. W.

The Preparation, Crystalline Structure, and Physical Properties of the Two Forms of Solid Nitroglycerin [Glyceryl Trinitrate]. HAROLD HIBBERT (*Eighth Inter. Cong. App. Chem.*, 1912, 4, 37—57).—The statement of Kast (A., 1906, i, 923) as to the existence of two isomeric forms of glyceryl trinitrate, m. p. 2.8° and 13.5° respectively, has been considerably discounted by the failure of Nauckhoff (A., 1912, i, 63) to isolate the more fusible isomeride.

It is now found that if a mixture of wood pulp or powdered glass wool with glyceryl trinitrate (preferably a fresh specimen which has not been previously solidified) is cooled to -40° , the latter crystallises in the new form described by Kast, for if glyceryl trinitrate at -40° is inoculated with it the whole crystallises to a *labile* form, m. p. 2.0° . This labile isomeride passes readily into the stable form, m. p. 13.1° , for although when fused and cooled again to -40° within one minute it spontaneously crystallises in the labile form, a longer period in the fused condition prevents any tendency to spontaneous crystallisation in any form. The solid labile form also passes rapidly into the stable one when inoculated with a trace of the latter or sometimes even on rubbing, the transformation being accompanied by a very appreciable development of heat; the labile form also appears to be the more sensitive towards shock.

If the wood pulp used for the initial freezing contains powdered sodium nitrate, inoculation with this mixture causes more rapid crystallisation of glyceryl trinitrate, but in the more stable modification. Potassium nitrate has no such effect on the nature of the solid which separates, and it is possible that the separation of the less fusible isomeride is not due merely to the presence of the sodium nitrate, but depends on other conjoint factors of which the presence of moisture is one.

Microphotographs are given of the crystals of the two forms, of which the labile belongs to the triclinic and the stable to the rhombic system. Attention is drawn to the remarkable analogy between the isomeric forms of glyceryl trinitrate and those of benzophenone (Zincke, this Journ., 1871, 24, 832; Auwers and Meyer, A., 1889, 611).

D. F. T.

Boiling Points of Solutions of Glyceryl Trinitrate. A. L. HYDE (*Eighth Inter. Cong. App. Chem.*, 1912, 4, 59—67).—Molecular-weight determinations have been effected by means of a modified form of the electrically heated Beckmann apparatus, with glyceryl trinitrate in various solvents; as the concentrations attained in some cases over 75 grams of the nitrate to 100 of solvent, the results calculated from the usual law for dilute solutions can hardly be very trustworthy. With ether, methyl alcohol or chloroform as solvent, the results indicate an association which increases with the concentration, whilst with acetone the results are below the theoretical. Ethyl acetate gave, over a fairly wide range of concentrations, concordant results, which agreed well with the theoretical molecular weight and its application for such determinations should be useful, for example, in the estimation of diglycerol tetranitrate admixed with glyceryl trinitrate. In a mathematical discussion of the results obtained with the three

solvents which give indications of association, it is shown that the rise in boiling point can be expressed by the equation $a = ch^n$, where a is the rise in b. p., h the percentage composition of the solution, whilst c and n are constants.

D. F. T.

Separation of Glyceryl Trinitrate from Nitro-substitution Compounds. A. L. HYDE (*Eighth Inter. Cong. App. Chem.*, 1912, 4, 69—76).—On shaking 1—3 grams of a mixture of glyceryl trinitrate and a nitro-derivative of toluene with 75 c.c. of carbon disulphide, four times with fresh portions (30 c.c.) of diluted acetic acid (65 acid : 35 water by volume), it is found that a fairly constant percentage of the nitrotoluene originally present in the mixture is left in the carbon disulphide, whilst the glyceryl nitrate is almost entirely to be found in the acetic acid. The quantity of nitrotoluene in the carbon disulphide is determined by careful evaporation after first washing the solution with water.

The following nitro-compounds were tried: *o*- and *p*-nitrotoluenes, liquid dinitrotoluene and its isomerides, m. p. 48° and 68° respectively, also liquid trinitrotoluene. Knowing the proportion of each of these to be found in the carbon disulphide after the above procedure, it is possible to apply this process to the rough estimation of any one of these nitro-compounds in a binary mixture with glyceryl trinitrate.

D. F. T.

Phytic Acid in Cottonseed Meal and Wheat Bran. J. B. RAJNER (*J. Amer. Chem. Soc.*, 1913, 35, 890—895).—The Patten and Hart modification of Posternak's method for the separation of inositol-phosphoric acid, or so-called phytic acid, from wheat bran gives a product containing at least 5% of inorganic impurity mainly iron and aluminium phosphates, so that the formula $C_{26}H_{50}O_{14}P_8$ based on such results is probably erroneous (compare Posternak, A., 1903, ii, 679). Examination of the phosphorus compounds of wheat bran which are soluble in 0.2% hydrochloric acid and of cottonseed meal which are soluble in similar acid and also extracted by subsequent treatment with 0.2% ammonium hydroxide, indicates that by purification they yield an identical acid $C_{26}H_{48}O_{14}P_8$; this on heating with sulphuric acid undergoes scission into inositol and phosphoric acid and it is free from pentosans.

D. F. T.

Trimethylene Trisulphide and Its Oxidation Products. OSCAR HINSBERG (*J. pr. Chem.*, 1913, [ii], 88, 49—58. Compare A., 1912, i, 546).—Trimethylene trisulphoxide dissolves in concentrated hydrochloric acid, yielding a compound which is resolved into its components on the addition of alcohol, and is considered to be a basic salt containing the group $CH_2 \cdot SCl \cdot OH$; when kept the solution deposits a colourless oil. In view of these results, the author is undertaking a study of the action of the halogen acids on the trisulphoxide, the present paper dealing particularly with the action of hydriodic acid.

Trimethylene trisulphoxide dissolves in warm dilute hydriodic acid and crystallises out again unchanged. When dissolved in concentrated

hydriodic acid (1 gram in 20—25 c.c., D=1.96) and the solution maintained for twenty-four hours at the ordinary temperature, the trisulphoxide is reduced to a new labile (β) *trimethylene trisulphide*, which is obtained as yellow, crystalline precipitate on diluting the solution with water. The new trisulphide has m. p. 247° (decomp.), and passes into the stable (α) trisulphide of m. p. 216° on crystallisation from chloroform, acetic acid, benzene or alcohol. Attempts to effect the reverse transformation by the action of acetyl chloride, ethyl iodide or iodine proved successful.

The β -trisulphide may also be prepared by dissolving the α -compound in concentrated hydriodic acid, and maintaining the solution for several days at the ordinary temperature.

A solution of trimethylene trisulphoxide in seven times its weight of hydriodic acid (D 1.96) deposits after twelve hours stout, brown plates or prisms of β -*trimethylene trisulphide tri-iodide*, $\text{CH}_2 \begin{smallmatrix} \text{SI} \cdot \text{CH}_2 \\ \text{SI} \cdot \text{CH}_2 \end{smallmatrix} \text{SI}$, which melts indefinitely at $118\text{--}123^\circ$ (decomp.), and loses its iodine completely when exposed to the air for eight days, or when heated at 60° , yielding β -trimethylene trisulphide. If the tri-iodide is crystallised from chloroform and then heated at 60° until the iodine is removed, either the pure α -trisulphide or a mixture of the α - and β -forms is obtained.

The tri-iodide combines with iodine in chloroform solution, yielding a *tetraiodide*, $\text{C}_3\text{H}_6\text{S}_3\text{I}_4$, which is derived from the α -trisulphide, and crystallises in elongated prisms, resembling iodine, m. p. 100° (decomp.), with previous sintering. The tetraiodide is more stable than the tri-iodide, but loses its iodine completely when heated for several hours at 60° , or when exposed to the air for several weeks yielding α -trimethylene trisulphide. If kept for several weeks in contact with aqueous sodium hydrogen carbonate, the tetraiodide loses only part of the iodine, with the formation of a brown substance which is probably the tri-iodide of α -trimethylene trisulphide.

The author has also investigated the action of hydrogen peroxide on the isomeric trisulphides, in the hope of obtaining the corresponding trisulphoxides, but no evidence of the existence of such isomerides was obtained.

When heated for two hours with 10—15% hydrogen peroxide on the water-bath, the trisulphides are converted into trimethylene trisulphoxide, which is accompanied by *trimethylenedisulphonesulphoxide*, $\text{CH}_2 \begin{smallmatrix} \text{SO}_2 \cdot \text{CH}_2 \\ \text{SO}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{SO}$.

The latter compound is separated from the trisulphoxide by taking advantage of its sparing solubility in water and organic solvents. It crystallises in colourless needles, which become brown at 270° without melting.

The action of hydrogen peroxide on the trisulphide also leads to the formation of *trimethylenedisulphidesulphide*, $\text{CH}_2 \begin{smallmatrix} \text{SO} \cdot \text{CH}_2 \\ \text{SO} \cdot \text{CH}_2 \end{smallmatrix} \text{S}$, which is readily soluble in water and crystallises in slender, colourless needles; m. p. about 210° (decomp.).

With respect to the isomerism of the trimethylene trisulphides, it is

pointed out that the existence of the two forms cannot be explained by a *cis-trans*-isomerism as in the case of the trithiobenzaldehydes, for, owing to the symmetrical structure of the molecule, stereoisomerism of this kind is excluded. The author inclines to the view that the isomerism is of a new type determined by spatial configuration of the sulphur atom, and suggests that the two modifications of trithiobenzaldehyde and of other substituted trithioformaldehydes may be sulphur isomerides of this type and not *cis-trans*-isomerides as usually imagined.

F. B.

Uranyl Formate. Reply to Courtois. WILLIAM ECHSSEUR DE CONINCK and ALBERT RAYNAUD (*Bull. Soc. chim.*, 1913, [iv], 13, 665—666. Compare this vol., i, 333).—A reply to Courtois (this vol., i, 585), in which the authors suggest that the salts used were different and that the experiments were conducted under different conditions.

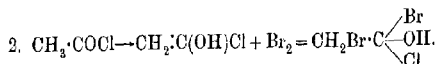
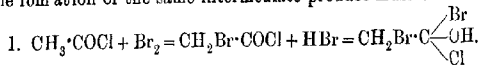
W. G.

The Mechanism of the Hell-Volhard Reaction. II. OSMAN ASCHAN [With (Frl.) ELLA EUROPAEUS] (*Ber.*, 1913, 46, 2162—2171. Compare A., 1912, i, 599).—Meyer (A., 1912, i, 941) expressed the opinion that the formation of a mixture of α -bromo-acid chloride and α -bromo-acid bromide by the action of bromine on acid chlorides is due, in the first place, to direct α -substitution, followed by a reaction between the liberated hydrogen bromide and the bromo-acid chloride, as in the equation: $\text{CH}_3\text{Br}\cdot\text{COCl} + \text{HBr} = \text{CH}_3\text{Br}\cdot\text{COBr} + \text{HCl}$.

The author now shows that anhydrous sulphuric acid does not react with acetyl chloride in the cold, and also describes the action of hydrogen chloride and bromide on the acid haloids. He finds that hydrogen bromide will convert acetyl chloride into acetyl bromide (compare Staudinger and Anthes, this vol., i, 616), but that, conversely, hydrogen chloride will transform acetyl bromide into acetyl chloride. Such changes cannot both be due to direct substitution, but are best explained by assuming the formation of the intermediate

compound, $\text{CH}_3\cdot\text{C}\begin{smallmatrix} \text{Br} \\ \diagup \\ \text{OH} \\ \diagdown \\ \text{Cl} \end{smallmatrix}$, which can part with either hydrogen chloride

or bromide, according to the conditions. Thus, whether it is assumed that direct α -substitution is the first step in the action of bromine on acid chlorides, or that enolisation of the carboxyl group takes place, the formation of the same intermediate product must be assumed.

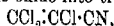


The following cases have been studied, and the amount of transformation that takes place during definite intervals of time, calculated from halogen estimations which were controlled by density determinations: the action of hydrogen bromide on acetyl chloride, chloroacetyl chloride and bromoacetyl chloride, and the action of hydrogen chloride on acetyl bromide, chloroacetyl bromide and bromoacetyl bromide. J. C. W.

Trichloroacrylic Acid and Certain of its Derivatives.

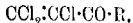
JACOB BÖESEKEN and P. DUJARDIN (*Rec. trav. chim.*, 1913, 32, 97—111).—Heptachloropropane, b. p. $115^{\circ}/12$ mm., obtained according to Prins' method (A., 1911, i, 173) by the action of chloroform on pentachloroethane in the presence of aluminium chloride, is converted by alcoholic potassium hydroxide into hexachloropropylene, b. p. $209-210^{\circ}/760$ mm., $99^{\circ}/15$ mm. (compare Fritsch, A., 1898, i, 63). The latter is conveniently converted into trichloroacrylic acid, m. p. 76° , by the action of slightly diluted sulphuric acid at 135° or by a boiling aqueous suspension of barium carbonate. The sodium, potassium, and magnesium salts of this acid are readily soluble, whilst the lead salt crystallises in leaflets sparingly soluble in water. From measurement of the conductivity, the acid appears to be dissociated to about the same extent as oxalic acid, whilst it has approximately the same influence on the rate of inversion of sucrose as hydrochloric acid in $\frac{1}{2}N$ -solution.

Trichloroacrylyl chloride, prepared by the action of an excess of thionyl chloride on the acid, has b. p. $158^{\circ}/760$ mm., n_D^{20} 1.52709, and when treated with ammonia in benzene solution is converted into the corresponding amide, m. p. 96° (compare Fritsch, *loc. cit.*). The latter is transformed by phosphoric oxide into trichloroacrylonitrile,

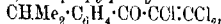


m. p. 20° , n_D^{20} 1.5100.

A series of mixed aromatic ketones of the general formula



has been prepared either by gradual addition of the benzenoid derivatives to the stable molecular compound, $\text{CCl}_2\text{:CCl}\cdot\text{COCl}\cdot\text{AlCl}_3$ (compare Böeseken and Hasselbach, this vol., i, 335), or by addition of the acid chloride to a mixture of benzenoid derivative and catalyst, reaction being continued only until one molecule of hydrogen chloride had been evolved. In this manner, the following ketones have been obtained: (i) *phenyl trichlorovinyl ketone*, b. p. $138^{\circ}/2$ mm., D_4^{20} 1.3902, n_D^{20} 1.5798, which unites with chlorine in sunlight to form pentachloropropiophenone, m. p. 82.5° (compare Böeseken and Hasselbach, *loc. cit.*); (ii) *p-chlorophenyl trichlorovinyl ketone*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{CCl}_2\text{CCl}_2$, b. p. $159^{\circ}/17$ mm., m. p. 19° , from trichloroacrylyl chloride and chlorobenzene. The isomeric *o*-chloro derivative could not be isolated from the product. When acted on by chlorine in sunlight, *p*-chlorophenyl trichlorovinyl ketone yields *p*-chlorophenyl pentachloroethyl ketone, white crystals, m. p. 116° ; (iii) *p-tolyl trichlorovinyl ketone*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CCl}_2\text{CCl}_2$, b. p. $147.5^{\circ}/10$ mm.; (iv) *m-xylol trichlorovinyl ketone*, b. p. $165^{\circ}/14$ mm.; (v) *p-xylol trichlorovinyl ketone*, b. p. $161^{\circ}/13$ mm.; (vi) *sec-propylphenyl trichlorovinyl ketone*,



b. p. $173^{\circ}/12$ mm. In the three latter cases, reaction is very vigorous, but seems also to proceed in another direction, since evolution of hydrogen chloride continues after the quantity corresponding to one molecule has been evolved. (vii) *ψ -Cumyl trichlorovinyl ketone*, $\text{C}_6\text{H}_5\text{Me}_2\cdot\text{CO}\cdot\text{CCl}_2\text{CCl}_2$, m. p. 57° . (viii) *p-Anisyl trichlorovinyl ketone*, m. p. 26.5° . In this case, the action is far less rapid than with toluene. Reaction was carried out in carbon disulphide solution when

a certain amount of the ketone was simultaneously decomposed with formation of *p*-hydroxybenzoic acid. (ix) *Phenetyl trichlorovinyl ketone*, m. p. 58°, D_4^{25} 1.3202, n_D^{25} 1.5736.

The position of the substituents in the above ketones is deduced from a study of their decomposition by alkali. When mixed with potassium alkoxides they are immediately decomposed with separation of the potassium salt of the aromatic acid according to the equation: $X \cdot C_6H_4 \cdot CO \cdot CCl_2CCl_2 + KOH = X \cdot C_6H_4 \cdot CO_2K + HCCl_2CCl_2$. In this manner, benzoic, *p*-toluic, anisic, *p*-ethoxybenzoic, and *p*-chlorobenzoic acids were obtained from phenyl trichlorovinyl ketone, *p*-tolyl trichlorovinyl ketone, *p*-anisyl trichlorovinyl ketone, *p*-phenetyl trichlorovinyl ketone, and *p*-chlorophenyl trichlorovinyl ketone respectively.

H. W.

Methylation of Aliphatic Compounds by means of Methyl Sulphate. EUGENE GRANDMOUGIN, EM. HAYAS and G. GUYOT (*Chem. Zeit.*, 1913, **37**, 812—813).—Although methyl sulphate has been extensively used in the methylation of aromatic substances, very few instances have been recorded of its use with aliphatic compounds. The authors have therefore investigated its applicability to the latter class and find that, in a series of typical methylations, this reagent can advantageously replace the customary methyl iodide under definite conditions of experiment.

Ethyl methylacetacetate is obtained in 85% yield by the gradual addition of methyl sulphate to a solution of ethyl sodioacetacetate in methyl alcohol under definite conditions of temperature which are fully described in the original, and, when again methylated under similar conditions, gives an 87% yield of ethyl dimethylacetacetate.

In an analogous manner, ethyl methylmalonate and ethyl dimethylmalonate may be prepared, the yield of the former being 80—85%. The latter substance can also be obtained directly from ethyl malonate, the most favourable proportions being ester (1 mol.), sodium (3 atoms) and methyl sulphate (3 mols.). Employment of the theoretical quantities leads to the formation of a mixture of mono-methyl- and dimethyl-malonic esters.

Phenylmethylpyrazolone can also be readily methylated by means of methyl sulphate. When methyl sulphate is slowly added to a solution of sodium methoxide and phenylmethylpyrazolone in methyl alcohol,

5-methoxy-1-phenyl-3-methylpyrazole, $\begin{matrix} N-NPh \\ | \\ CMe \cdot CH \end{matrix} > C \cdot OMe$, is obtained

(compare Knorr, A., 1895, i, 397; von Pechmann, A., 1895, i, 454). When, on the other hand, methylation is accomplished by the addition of methyl sulphate to a boiling solution of sodium hydroxide in the minimum quantity of water and methylphenylpyrazolone in methyl alcohol, antipyrine is obtained in 80% yield.

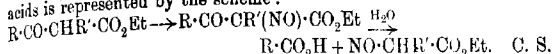
The conversion of aminoantipyrine into pyrimidone can also be readily effected by means of methyl sulphate.

H. W.

Aliphatic Nitrosocarboxylic Esters. JULIUS SCHMIDT and EMIL AECKERLE (*Annalen*, 1913, **398**, 251—256).—*Ethyl chloromethylacetacetate*, $CH_3 \cdot CO \cdot CMeCl \cdot CO_2Et$, b. p. 116—117°/75 mm, D_4^{25} 1.167,

n_D^{18} 1.4382, obtained from ethyl methylacetoacetate and sulphuryl chloride, is not attacked by nitrous fumes at 0°. Ethyl α -benzoylpropionate is converted by careful treatment with nitrous fumes at 0° into ethyl α -nitroso- α -benzoylpropionate, $C_6H_5 \cdot CO \cdot CMe(NO) \cdot O_2Et$, a dark blue liquid, n_D^{18} 1.4902, which exhibits oxidising properties, and gradually decomposes into benzoic acid and ethyl α -nitrosopropionate.

These two experiments indicate that the formation of nitrosocarboxylic esters by the action of nitrous fumes on the esters of alkylated ketonic acids is represented by the scheme:



Ricinstearolic Acid. GEORG MÜHLE (*Ber.*, 1913, 46, 2091—2098).—The presence of the triple linking in ricinstearolic acid is confirmed by the addition of iodine which occurs when the acid is treated with the calculated quantity of iodine and a trace of dried ferrous iodide in carbon disulphide or warmed with an acetic acid solution of iodine, the temperature being kept, however, below 40°; the resultant *ricinstearolic acid di-iodide*, $CH_3Me[CH_2]_4 \cdot CH(OH) \cdot CH_2 \cdot C \equiv C \cdot [CH_2]_2 \cdot CO_2H$, forms colourless needles, m. p. 62°, decomp. at 175°; sodium and barium salts, colourless needles; mercury salt, yellow powder; methyl ester, pale yellow oil, decomp. at 150°.

Ricinstearolic acid, needles, m. p. 51°, b. p. 260°/10 mm. without decomposition, obtained by successive treatment of castor oil with bromine and potassium hydroxide solution, is accompanied by a small quantity of *tri- α -trihydroxystearic acid*, m. p. 110—111°.

$CH_3Me[CH_2]_4 \cdot CH(OH) \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot [CH_2]_2 \cdot CO_2H$, identical with the α -isotrihydroxystearic acid obtained earlier by oxidation of castor oil. A specimen of ricinstearolic acid kept for twenty years without any precautions for the exclusion of atmospheric moisture gave a deposit of a *dihydroxystearic acid*, leaflets, m. p. 140—141°. The author was unable to reproduce the results of earlier workers, who state that on distillation of ricinelaic acid and of ricinoleic acid under reduced pressure, an acid, $C_{18}H_{32}O_2$, is produced.

Acetylricinelaic acid, obtained by acetylation of ricinelaic acid with acetic anhydride, is a bright yellow, viscid oil; *acetylricinstearolic acid* is very similar.

Methyl ricinstearolate, obtained by esterification with a methyl alcoholic solution of hydrogen chloride, or in alkaline solution with methyl sulphate, is a colourless oil, b. p. 225°/12 mm., D 0.9389; ethyl ester, b. p. 230°/12 mm., D 0.9371.

Glyceryl monoricinstearolate, obtained from α -monochlorohydrin and dried sodium ricinstearolate at 150°, is a pale yellow, viscid oil; *glyceryl triricinstearolate*, from trichlorohydrin and sodium ricinstearolate at 190—200° under pressure, is of similar appearance.

The action of phosphorus pentachloride on ricinstearolic acid in the cold, yields a chlorostearolic acid, $C_{18}H_{31}O_2Cl$, a pale yellow, viscid oil, which cannot be distilled without decomposition. D. F. T.

Thorium Chloro-oxalate. A. COLANI (*Compt. rend.*, 1913, 156, 1907—1909. Compare A., 1913, i, 444; Hauser and Wirth, A., 1913, i, 827).—Hauser and Wirth's method is the most convenient for

the preparation of this salt, which has the composition assigned to it by Wyruboff and Verneuil (A., 1899, ii, 598; compare Kohlschütter, A., 1902, i, 11). The behaviour of thorium oxalate with hydrochloric acid of various strengths at various temperatures is shown by lists of analytical results in the original. The chloro-oxalate loses from 0.5 to 1.00% of thorium by volatilisation of the chloride when heated rapidly, but no loss takes place when heat is gradually applied and the thoria, produced under the latter conditions, contains only 0.1 to 0.2% of chlorine. Similarly, thorium oxalate precipitated in solutions of moderately concentrated hydrochloric acid contains very little chlorine. In these two respects, thorium behaves differently from the rare earths. Determinations of the solubility of thorium chloro-oxalate in hydrochloric acid are given in the original, and show that the solubility is much diminished in presence of oxalic acid, but that in the absence of the latter and with liquids containing 21.2% or less of hydrogen chloride, decomposition is rapid and complete into oxalate and chloride.

T. A. H.

Barium Malonate Jellies and their Micro-structure. FRIEDRICH FLADE (*Zeitsch. anorg. Chem.*, 1913, 82, 173—191).—The transformation of barium malonate jellies into powders takes place more slowly than with other barium salts (compare Neuberg and Neimann, A., 1906, ii, 753; Neuberg and Rewald, A., 1908, ii 39).

Equivalent quantities of solutions of malonic acid and barium hydroxide in methyl alcohol and glycerol are freed from air-bubbles by placing under an exhausted bell-jar and mixed. The greater the proportion of glycerol, the slower the formation of the jelly. If the glycerol is removed by means of methyl alcohol, it may be replaced by other liquids, such as chloroform or benzene, without destruction of the jelly, and with a great increase in its transparency. Much of the liquid may be removed by pressure between filter-paper, or by evaporation. The residue is barium malonate with $2\text{H}_2\text{O}$. Warming does not liquefy the jelly.

Microscopical observations show that the jelly is made up of a network of fibres of barium malonate, in which the liquid is held as in a sponge. These fibres are stained deeply by methyl violet. The fibres are about 0.5 mm. long and 0.0001—0.0003 mm. thick, and are shown to be crystalline by their behaviour in polarised light.

C. H. D.

Stereochemistry of the Halogen Substituted Succinic Acids. BROR HOLMBERG (*J. pr. Chem.*, 1913, [ii], 87, 456—479).—The author has shown previously (A., 1912, i, 603) that during the hydrolysis of the sodium salt of *l*-bromosuccinic acid, the elimination of bromine proceeds at a greater rate than the increase in the acidity of the solution, and from these results has drawn the conclusion that the formation of malic acid from the bromo-acid is preceded by the formation of propiolactonecarboxylic acid.

The present paper deals with conditions favourable to the formation of the lactone and also with the hydrolysis of the sodium salts of, *l*-chlorosuccinic, *l*-iodosuccinic and *l*-bromosuccinic acids. In the case of bromosuccinic acid, the addition of neutral salts of weak acids

(formate, acetate, succinate and malate) increases the velocity of bromine ion formation, but diminishes the rate of hydrolysis of the lactone. Further, the formation of the lactone proceeds less readily with chlorosuccinic and bromosuccinamic acid than with bromosuccinic acid.

It is also found that the hydrolysis of the lactone yields either a *l*- or *d*-malic acid accordingly as it is carried out in acid or alkaline solution. Thus, a solution of *l*-bromosuccinic acid after being exactly neutralised with sodium hydroxide was maintained for twenty-four days at 25°, and then contained 10% of unchanged bromo-acid, 25% of lactone and 65% of malic and fumaric acids; after the bromo-acid and lactone had been completely hydrolysed by heating the solution on the water-bath, the malic acid obtained from the product was levorotatory. On the other hand, when the hydrolysis was effected by excess of sodium hydroxide, the resulting malic acid contained a preponderance of the dextrorotatory form.

Similar results were obtained in the case of silver oxide; the action of excess of the oxide on *l*-bromosuccinic acid yields a dextrorotatory malic acid, whilst the theoretical amount necessary to form the neutral silver salt gives rise to a levorotatory acid.

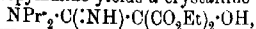
F. B.

Symmetric and Asymmetric Acid Dichlorides. II. ERWIN OTT (*Ber.*, 1913, 46, 2172—2175. Compare A., 1912, i, 828).—A further difference in reactivity between symmetric and asymmetric chlorides is in their behaviour on treatment with hydrogen and platinum black. Whereas fumaryl and chlorofumaryl chlorides immediately "poison" the catalyst so that not even limonene can be reduced in their presence, chloromaleyl chloride may easily be reduced to *n*-butyric acid. The hydrogen chloride which is formed gradually impedes the reduction, but if it is removed from time to time by evacuation, the absorption of hydrogen can be carried almost to the theoretical value. The reduction of dibromomaleyl chloride, however, could only be carried to one-fifth before "poisoning" of the platinum took place, whilst *as-o*-phthalyl chloride and phthalyl tetrachloride could not be reduced at all.

J. C. W.

Ethyl Cyanotartrate and its Reactions with Amines. RICHARD SYDNEY CURTISS and LLOYD F. NICKELL (*J. Amer. Chem. Soc.*, 1913, 35, 885—890. Compare Curtiss and others, A., 1911, i, 353, 366; A., 1909, i, 763).—The reaction between anhydrous hydrogen cyanide and ethyl oxomalonate is greatly influenced by small variations in temperature; at 30° it is complete in twenty-four hours, the product being *ethyl cyanotartrate*, $\text{OH}\cdot\text{C}(\text{CN})(\text{CO}_2\text{Et})_2$, an undistillable oily liquid, D_{20}^{25} 1.16; it is soluble in alkaline solutions to a yellow solution, and if treated in ether with sodium, deliquescent, colourless crystals of an unstable substance slowly separate.

Ethyl cyanotartrate in cooled ethereal solution reacts with many amines, producing compounds which in all probability have an amidine structure; thus dipropylamine yields a crystalline substance,



m. p. 72.5—73°. With diethylamine an analogous compound, m. p. 56°, was obtained, whilst benzylamine gave in a similar manner a

substance, m. p. 55–56°. These three substances on exposure to the atmosphere or when kept at 25°, undergo decomposition with formation of a tarry mass. Ethylamine, isobutylamine and benzylethylamine gave rise to uncrystallisable syrups, triethylamine slowly produced a red, tarry mass, whilst ammonia formed a very unstable, crystalline substance. With aromatic amines there was apparently no reaction.

D. F. T.

Catalytic Decomposition of Aldehydes. M. I. KUZNECOW (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 557–568).—In his earlier experiments on the oxidation of methyl alcohol by means of atmospheric oxygen with a view to preparing formaldehyde, the author found that the aldehyde was always accompanied by carbon monoxide and hydrogen in proportions depending on the temperature conditions and on the nature of the catalyst employed (*Bull. Charkov Technol. Inst.*, 1909). These two products result from the decomposition of aldehyde previously formed: $\text{CH}_2\text{O} = \text{CO} + \text{H}_2$.

Further experiments show that resolution of the aldehydic group with formation of carbon monoxide is a general reaction for all aldehydes.

The first series comprises measurements of the degree of decomposition of formaldehyde at various temperatures and under the influence of a number of different metals and of wood charcoal, asbestos and powdered Jena glass. The results show that the action depends not only on the chemical character of the catalyst but also on its physical condition. For instance, with copper turnings at 500° there is no decomposition, and at 600° only 4% of the aldehyde is attacked; with copper reduced from the oxide by the action of hydrogen, 9.2% of the aldehyde is decomposed at 500°; and with copper obtained by reduction of copper sulphate solution by means of alkaline formaldehyde, the action proceeds to the extent of 35.3, 84.2, 94.8 and 95.8% at 200°, 300°, 400° and 500° respectively. With different forms of other metals smaller variations are observed.

In the second series the products obtained by the decomposition of the following aldehydes by palladium black were investigated: formaldehyde, acetaldehyde, paracetaldehyde, propaldehyde, *n*-butaldehyde, isobutaldehyde, benzaldehyde and *p*-tolualdehyde. The results show that the aldehyde group is decomposed by palladium into carbon monoxide and hydrogen, the latter combining with the hydrocarbon radicle: $\text{R}\cdot\text{CHO} = \text{RH} + \text{CO}$. In the cases of propaldehyde and the butaldehydes, free hydrogen and unsaturated hydrocarbons are also obtained owing to the partial decomposition of the saturated hydrocarbons originally formed.

T. H. P.

Stability of Paracetaldehyde. R. RICHTER (*Pharm. Zeit.*, 1913, 58, 482–483).—A series of experiments has been performed on the stability of paracetaldehyde alone, in aqueous solution and in the presence of various pharmaceutical preparations. The author is led to the following conclusions: (1) pure paracetaldehyde, free from acid and acetaldehyde, can be kept for sixteen months without alteration; the presence of these substances even in small quantity,

however, induces a gradual decomposition of the paracetaldehyde; (2) in the presence of pure raspberry juice without addition of water, paraldehyde remains unchanged during two months; (3) when mixed with water and a syrup composed of sugar and citric acid, paracetaldehyde speedily undergoes conversion into acetaldehyde; after two months, 7.8% of the paracetaldehyde had undergone such conversion; (4) in aqueous solution, without addition of juice, formation of acetaldehyde occurs slowly but continuously.

H. W.

Catalytic Actions. VII. Polymerisation of Chloral. JACOB BOESEKEN and A. SCHIMMEL (*Rec. trav. chim.*, 1913, 32, 112—127).—The authors have studied the polymerisation of chloral in the presence of pyridine. For this purpose, known weights of dry chloral and pyridine have been preserved for a month at the ordinary temperature, at the end of which time a quasi-stable state had been reached. The contents of the flask were then treated with a large quantity of dilute hydrochloric acid, which combined with the pyridine and dissolved unchanged chloral. The metachloral which is insoluble in this reagent was estimated by decomposition with potassium hydroxide.

As the quantity of pyridine employed relatively to the amount of chloral increases, the latter becomes more completely transformed into metachloral, until, in the presence of about $\frac{1}{12}$ mol. pyridine, transformation is practically quantitative. Beyond this point, the amount of metachloral formed diminishes with increasing quantities of pyridine. The separation of metachloral is incomplete, whatever the quantity of catalyst employed. From determinations of the vapour tension of metachloral, obtained from chloral either by means of pyridine or fuming sulphuric acid, it appears that the true equilibrium of the system, chloral \rightleftharpoons metachloral, is situated practically entirely on the side of metachloral, and thus, that starting from chloral, this equilibrium is not obtained after a month even in the presence of considerable quantities of catalyst. This result is probably due to the absorption of pyridine by the polymeride which separates in the colloidal state.

When pyridine (4—5 mols.) is added to chloral (100 mols.) a rapid separation of a gelatinous mass occurs. After several weeks, a second change is observable in that the metachloral in contact with the walls of the vessel again becomes transparent, forming a membrane greatly resembling a collodion pellicle. This transparent metachloral does not appear to retain pyridine and has a vapour tension below that of the equilibrium mixture.

When pure metachloral is placed in an atmosphere of pyridine, it almost immediately becomes opaque, and then has the same vapour tension as the pseudo-binary system. Subsequently, it becomes gelatinous and then completely liquid.

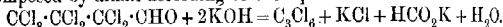
In the presence of larger quantities of catalyst, less chloral is transformed into the polymeride, although equilibrium is more certain to be obtained in this case since a portion of the metachloral dissolves in the pyridine. The catalyst here exerts a marked influence on the

equilibrium, although it has not been found possible to isolate an additive compound of pyridine and chloral.

The phenomena here observed are analogous to those encountered in the polymerisation of chloral by means of fuming sulphuric acid (Bösesken, *Rec. trav. chim.*, 1910, 29, 104) or aluminium chloride.

H. W.

Modifications of Metachloral and Decomposition of Chloral by Aluminium Chloride. Perchlorobutanal, $\text{CCl}_3\cdot\text{CCl}_2\cdot\text{CCl}_2\cdot\text{CHO}$, JACOB BOESEKEN and A. SCHIMMEL (*Rec. trav. chim.*, 1913, 32, 128—133).—Metachloral is known in a gelatinous modification immediately obtained by the addition of pyridine to anhydrous chloral, an opaque modification formed by the action of different catalysts on chloral, and representing the equilibrium mixture of the system $\text{chloral} \rightleftharpoons \text{metachloral}$ and as a transparent modification which is slowly produced when pyridine remains in contact with chloral. The latter is probably the only pure metachloral, the others being mixtures of it with unchanged chloral and catalyst. Attempts have been made to obtain the polymeride of chloral described by Combes (*A.*, 1887, 127) as the product of the action of aluminium chloride on chloral. The authors have repeated his experiments, and have also somewhat modified the conditions, and find that the products are tetrachloroethylene, pentachloroethane and relatively very small amounts of perchlorobutanal, b. p. 145.5—147°/20—26 mm., m. p. 46.5—48°, molecular weight in benzene solution, 334. The latter is quantitatively decomposed by alkali according to the equation :



When heated with excess of aluminium chloride, it is decomposed with evolution of carbon monoxide.

H. W.

The Catalytic Preparation of Ketones. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1913, [iv], 13, 666—671).—A reply to Senderens (*A.*, 1911, i, 134, 302; this vol., i, 342) in which the author maintains the utility of his method using zinc oxide, and more especially cadmium oxide, as a catalyst in the preparation of ketones from acids. W. G.

Cerium Acetylacetonates. ANDRÉ JOB and PAUL GOISSEDET (*Compt. rend.*, 1913, 157, 50—52).—Urbain (compare *A.*, 1897, i, 236) prepared a basic cerous acetylacetonate by the action of cerous hydroxide on acetylacetone, and Biltz (compare *A.*, 1904, i, 715) obtained the crystalline, neutral cerous salt by the action of cerous nitrate on an ammoniacal solution of ammonium acetylacetonate. Adopting Urbain's method the author has now prepared the ceric compound in a crystalline state. An excess of acetylacetone is added to a suspension of ceric hydroxide in water and the mixture agitated, when it slowly turns brown, and at the end of several days deep red needles of ceric acetylacetonate separate, having the composition $\text{Ce}(\text{CHAc}_2)_4 \cdot 11\text{H}_2\text{O}$. On drying this salt in a vacuum and crystallising it from carbon tetrachloride, it is obtained in the anhydrous state as black crystals, m. p. 171—172°, having a metallic lustre. It is slightly soluble in water, and in solution is readily hydrolysed except

in the presence of excess of acetylacetone. The anhydrous salt is soluble in most organic solvents to a deep red solution, the colour rapidly disappearing in sunlight in the case of oxidisable solvents.

W. G.

Syntheses by means of Sodamide. II. Alkylation of Aliphatic Ketones. ALBIN HALLER and EDOUARD BAUER (*Ann. Chim. Phys.*, 1913, [viii], 29, 313—349).—The authors' work (A., 1909, i, 108) on the alkylation of acetophenone and analogous substances by the successive action of sodamide and alkyl haloids has been extended to aliphatic ketones.

When an ethereal solution of pinacolone is treated successively with sodamide (1 mol.) and methyl iodide (1.1 mol.), a mixture of unchanged material, methyl- and dimethyl-pinacolone is obtained from which $\beta\beta$ -dimethylpentan- γ -one, $\text{CMe}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_3$, b. p. 124—126°, can be isolated by repeated fractional distillation. This substance has already been described by Wischnegradsky (A., 1875, 878). The oxime has m. p. 79—80°. When the methylation is repeated until no further action occurs in ethereal solution, $\beta\beta\beta$ -trimethylpentan- γ -one, $\text{CMe}_3\cdot\text{CO}\cdot\text{CHMe}_2$, b. p. 133—135° (compare Nef, A., 1900, i, 349), is obtained. It has D_4^{20} 0.80536, n_D^{20} 1.40304, n_D^{25} 1.40513, n_D^{30} 1.41020, n_D^{35} 1.41429. The oxime has m. p. 141°. When reduced by sodium and alcohol, the ketone yields $\beta\beta\beta$ -trimethylpentan- γ -ol, $\text{CMe}_3\cdot\text{CH}(\text{OH})\cdot\text{CHMe}_2$.

b. p. 145—148°, the *phenylurethane* of which has m. p. 79°. $\beta\beta\beta$ -Trimethylpentan- γ -one can be further methylated by means of sodamide and methyl iodide in benzene solution, when $\beta\beta\beta\delta$ -tetramethylpentan- γ -one, $\text{CMe}_3\cdot\text{CO}\cdot\text{CMe}_3$, is obtained. It has b. p. 150—151°, D_4^{20} 0.81992, n_D^{20} 1.41485, n_D^{25} 1.41702, n_D^{30} 1.42224, n_D^{35} 1.42643. It does not appear to form an oxime, a semicarbazone or a hydrazone. Its ketonic nature is, however, established by reducing it to $\beta\beta\beta\delta$ -tetramethylpentan- γ -ol, b. p. 165—166°, m. p. 50°, the *phenylurethane* of which has m. p. 118—119°, whilst the *formate* has b. p. 185°. In a similar manner, pentamethylacetone can be converted into $\beta\beta\beta\delta\delta$ -tetramethylhexan- γ -one, $\text{CMe}_3\cdot\text{CO}\cdot\text{CMe}_2\text{Et}$, b. p. 172—174°, by the successive action of sodamide and ethyl bromide or iodide in benzene solution. Like its lower homologue, this substance forms neither oxime, semicarbazone or hydrazone. Reduction converts it into $\beta\beta\beta\delta\delta$ -tetramethylhexan- γ -ol, $\text{CMe}_3\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\text{Et}$, b. p. 187—188°, the *phenylurethane* of which forms slender needles, m. p. 94—95°.

The ethylation of pinacolone can be effected in a precisely similar manner. The successive action of sodamide and ethyl bromide or iodide on an ethereal solution of pinacolone leads to the isolation of $\beta\beta$ -dimethylhexan- γ -one, $\text{CMe}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\text{Me}$, b. p. 146—148°, D_4^{20} 0.81055, n_D^{20} 1.40740, n_D^{25} 1.40952, n_D^{30} 1.41465, n_D^{35} 1.41888, and $\beta\beta$ -dimethyl- δ -ethylhexan- γ -one, $\text{CMe}_3\cdot\text{CO}\cdot\text{CHEt}\cdot\text{CH}_2\text{Me}$, b. p. 174—176°, D_4^{20} 0.82521, n_D^{20} 1.42007, n_D^{25} 1.42227, n_D^{30} 1.42738, n_D^{35} 1.43173. The former yields an oxime, needles, m. p. 76—77°, and on reduction gives $\beta\beta$ -dimethylhexan- γ -ol, b. p. 155—157° (*phenylurethane*, m. p. 70—71°). The latter does not combine with hydroxylamine or with semicarbazide, but, when reduced with sodium and absolute alcohol, forms

$\beta\beta$ -dimethyl- δ -ethylhexan- γ -ol, b. p. 187°, the phenylurethane of which crystallises with $\frac{1}{2}$ H₂O and has m. p. 107°. In benzene, or better in toluene solution, complete ethylation of pinacolone can be effected, whereby $\beta\beta$ -dimethyl- $\delta\delta$ -diethylhexan- γ -one, b. p. 214—216°, is produced. It does not yield an oxime or a semicarbazone. Reduction converts it into $\beta\beta$ -dimethyl- $\delta\delta$ -diethylhexan- γ -ol, $\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CEt}_2$, b. p. 226—228°, the phenylurethane of which has m. p. 110°.

$\beta\beta\delta$ -Trimethylhexan- γ -one, $\text{CMe}_3\cdot\text{CO}\cdot\text{CHMeEt}$, b. p. 155—156°, is obtained mixed with unchanged starting material by the methylation of ethylpinacolone in ethereal solution. Since a separation of the two could not be effected by distillation, the product was treated with an alcoholic solution of hydroxylamine hydrochloride with which only the latter reacted to form an oxime. The mother liquors, separated as completely as possible from the crystalline oxime, were acted on by phenylcarbimide, whereby the dissolved oxime was converted into carbanilidoxime, which remained on distilling the mixture under diminished pressure. The distillate was treated with water to decompose the excess of phenylcarbimide, and the ketone extracted with ether and distilled. When reduced, it is converted into $\beta\beta\delta$ -trimethylhexan- γ -ol, $\text{CMe}_3\cdot\text{CH}(\text{OH})\cdot\text{CHMeEt}$, b. p. 169°, the phenylurethane of which has m. p. 78°.

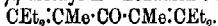
* $\beta\beta\epsilon$ -Trimethylhexan- γ -one, $\text{CMe}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHMe}_2$ (compare Nef, A., 1902, i, 6), is obtained in the usual manner as a liquid, b. p. 157·5—158·5°. Its oxime has m. p. 77—78°, whereas Nef gives 66—70°.

Although the action of allyl iodide on the sodium derivative of acetophenone yields only complex resinous products, allylpinacolones can be readily obtained by the successive action of sodamide and allyl iodide on an ethereal solution of pinacolone. In this manner, allylpinacolone, $\text{CMe}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$, b. p. 61—64°/14 mm., and diallylpinacolone, $\text{CMe}_2\cdot\text{CO}\cdot\text{CH}(\text{CH}_2\cdot\text{CH}:\text{CH}_2)_2$, b. p. 83—86°/14 mm., are readily prepared.

δ -Benzyl- $\beta\beta$ -dimethyl- δ -ethylhexan- γ -one, $\text{CMe}_2\cdot\text{CO}\cdot\text{CEt}_2\cdot\text{CH}_2\text{Ph}$, is obtained by the action of benzyl chloride on a boiling solution of the sodium derivative of diethylpinacolone in toluene. It has b. p. 152—154°/15 mm., and does not yield an oxime or a semicarbazone.

In the cases of pinacolone and of acetophenone, a tertiary carbon atom is attached to the carbonyl group. The authors have therefore extended their investigations to such ketones in which this is not the case, and find that alkylation can be similarly effected, substitution occurring at either of the secondary carbon atoms attached to the keto-group (compare Haller, A., 1905, i, 214; Haller and Bauer, A., 1912, i, 269).

An ethereal solution of diethyl ketone reacts vigorously with sodamide, and, after addition of methyl iodide, yields, on fractionation, ethyl isopropyl ketone, $\text{COEt}\cdot\text{CHMe}_2$, b. p. 115—119°, di-isopropyl ketone, $\text{CO}(\text{CHMe}_2)_2$, b. p. 123—124·5° (semicarbazone, m. p. 143—144°), and a fraction, b. p. 148—152°/18 mm., which is probably $\delta\epsilon$ -dimethyl- $\gamma\eta$ -diethyl- Δ^5 -nonadien- ϵ -one,

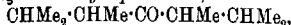


$\beta\delta\delta$ -Trimethylhexan- γ -one, b. p. 158—161°, is prepared by the

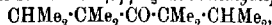
ethylation of di-isopropyl ketone in etherum solution. It does not yield an oxime or a semicarbazone. On reduction it gives $\beta\delta\delta$ -trimethylhexan- γ -ol, $\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{Et}$, b. p. 170—171°, the phenylurethanes of which has m. p. 64°. $\gamma\gamma\epsilon\epsilon$ -Tetramethylheptan- δ -one, $\text{CMe}_2\cdot\text{Et}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{Et}$,

prepared by the ethylation of isopropyl *tert.*-amyl ketone in benzene solution, has b. p. 196—198°, and does not give an oxime or a semicarbazone. Sodium and absolute alcohol convert it into $\gamma\gamma\epsilon\epsilon$ -tetramethylheptan- δ -ol, b. p. 210—212° (phenylurethane, m. p. 62—63°).

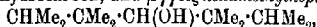
By repeated methylation of isovalerone in benzene solution and subsequent fractional distillation, the following products have been obtained: (i) $\beta\gamma\epsilon\epsilon$ -tetramethylheptan- δ -one,



b. p. 76—78°/13 mm., which, when energetically treated, appears to yield small quantities of the corresponding oxime; (ii) $\beta\gamma\gamma\epsilon\epsilon$ -pentamethylheptan- δ -one, $\text{CHMe}_2\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{CHMe}_2$, b. p. 88—89°/13 mm., which does not yield an oxime when heated with Crismer's reagent in alcoholic solution. $\bullet\beta\gamma\gamma\epsilon\epsilon\epsilon$ -Hexamethylheptan- δ -one,



b. p. 107—109°/14 mm., is prepared by the methylation of trimethylisovalerone in toluene solution. When reduced with sodium and alcohol, it yields a small quantity of a substance which behaves like an unsaturated hydrocarbon, and $\beta\gamma\gamma\epsilon\epsilon\epsilon$ -hexamethylheptan- δ -ol,



b. p. 115—117°/13 mm. (phenylurethane, m. p. 91—92°).

H. W.

Optically Active Complex Glucinum Sugar Compounds.

BENNO BLEYER and L. PACZUSKI (*Zeitsch. physikal. Chem.*, 1913, 84, 1—14).—The authors have determined the influence of an alkaline solution of glucinum hydroxide on the rotatory power of mannitol. It is shown that when an alkaline solution of glucinum hydroxide is added to a solution of inactive mannitol, the solution becomes markedly levorotatory. The influence of the alkaline glucinum solution is shown to depend on the presence of GlO_2^- ions in the solution, that is, it is due to sodium glucinate. The presence of glucinum hydroxide as a colloid could not produce so large a change in the rotation. A method is worked out, depending on the change of rotation, for determining the relative strength of the acid in amphoteric metal hydroxides. On adding solutions of sodium glucinate to mannitol, a condition is reached at which a constant rotation is reached; further additions cannot change this in either sense. This condition is reached when the concentration 13.84 grams mannitol, 72 grams sodium hydroxide, and 56.64 grams of glucinum sulphate per litre of solution is reached. A complex compound is formed by the action of sodium glucinate on mannitol, which is not hydrolysed at the concentrations examined, (1/640—10/640)*N*. This compound is similar to the complex glucinum hydroxydicarboxylic acid of Rosenheim and Itzig (*A.*, 1899, i, 739).

J. F. S.

Unfermentable Residue in Hydrolytic Products of Starch. ARTHUR P. BRYANT and C. S. MINER (*Eighth Intern. Cong. App. Chem.*, 1912, 13, 57—61).—Results are recorded which tend to show that some of the hydrolytic products of starch, such as "grape-sugar" and "liquid glucose," contain isomaltose. W. H. G.

Presence of Maltose in Acid Hydrolysed Starch Products. GEORGE DEFREN (*Eighth Intern. Cong. App. Chem.*, 1912, 13, 111—112).—It has been found possible to isolate maltose from a crude glucose obtained by the hydrolysis of starch with acids. The dextrose present in the crude product was removed by fermentation, making use of *Saccharomyces apiculatus*, and the dextrin separated from the maltose subsequently by fractional precipitation with alcohol. W. H. G.

Hydrolysis of Starch by Acids with Some Additional Results on the Speed of Hydrolysis. GEORGE DEFREN (*Eighth Intern. Cong. App. Chem.*, 1912, 13, 113—123).—An investigation on the hydrolysis of starch by acids. The relative speeds of hydrolysis using hydrochloric, sulphuric, oxalic, sulphurous and acetic acids are given, likewise results which show the effect of the concentration of the acid and the temperature on the rate of hydrolysis. The increase in the rate of hydrolysis with rise of temperature above 100° is very great, indicating that the starch molecule becomes very "labile" at these temperatures. W. H. G.

Osmotic Pressure of Colloids. V. Colloid Chemistry of the Dextrins. WILHELM BILTZ (and WILHELM TRUTHE) (*Zeitsch. physikal. Chem.*, 1913, 83, 683—707. Compare A., 1910, ii, 22, 673; 1911, ii, 702; this vol., i, 593).—The molecular weight of a number of dextrins is determined by extrapolation to concentration zero from the calculated molecular weights obtained from the measurement of the osmotic pressure of dilute solutions. It is shown that even in dilute solutions the dextrins associate very markedly. The following values are found for the molecular weights: amylopectin (a) 22200, amylopectin (b) 20500, achroodextrin 10200, diastase dextrin (from grain) 11760, diastase dextrin (from beer) 8200, erythropectin 6800, erythropectin IIa 3000, acid dextrin 4000, achroodextrin I 1800, achroodextrin II 1200, dextrin β 950, sucrose 340, commercial dextrin (2 specimens) 5000, 6000, specially purified commercial dextrin 2800 and 2700, dextrin purified by dialysis 6200. The gold numbers of the various dextrins are determined, and it is shown that a relationship exists between the molecular weight and the gold number; generally a small gold number accompanies a large molecular weight. The authors have shown that in many cases the dextrins possess more than one gold number, and that there is an oscillating protecting action of the colloid between given concentrations. The viscosity of the dextrins in dilute solutions, that is, up to 5%, is determined, and it is shown that a parallelism exists between the viscosity and the molecular weight. It is also shown that the higher the molecular weight, the more the dextrins are adsorbed by ferric hydroxide gels. J. F. S.

Hydrolysis and Acetolysis of Cellulose. HERMANN OST (*Annalen*, 1913, 398, 313—343. Compare this vol., i, 446).—The composition of the hydrocelluloses obtained as the initial product of the hydrolysis of cellulose by dilute mineral acids has long been a matter of dispute. The author finds that cellulose can be dried completely, without discoloration, by heating slowly to 100° and finally at 120—125°; the same is true of hydrocelluloses, some specimens of which, however, become discoloured at 125—150°. Since the ultimate analysis of completely dried cellulose and hydrocelluloses fails to disclose any differences in the percentages of carbon and of hydrogen, the author abandons his previous views that hydrocelluloses are hydrated celluloses, and inclines to Stern's opinion (T., 1904, 85, 336) that there is no difference in the composition of celluloses and hydrocelluloses. The molecular magnitude of the latter is the smaller, as is indicated, not only by the smaller viscosity of their solutions, but also by their greater reducing action on copper salts, hydroxyl or aldehyde-groups being produced during the hydrolysis of the cellulose.

The acetolysis of cellulose is described in detail, the conditions under which cellobiose octa-acetate or dextrose α -penta-acetate (Ost, *loc. cit.*) are produced being definitely determined. The uncrystallisable syrup obtained in the acetolysis of cellulose resembles that obtained in the acetolysis of dextrose in acetic acid content, in rotatory power, and in yielding crystallised dextrose α -penta-acetate by further acetylation. Both syrups consist essentially of dextrose acetates mixed with acetates of isomaltose and dextrans and of other foreign substances.

The total yield of dextrose and cellobiose acetates obtained by the acetolysis of cellulose is 90% of that theoretically possible. Acetolysis, therefore, furnishes another proof that the cellulose molecule is composed only of dextrose residues. C. S.

Absorption Spectra of the Copper Derivatives of Primary Aliphatic Nitroamines. ANTOINE P. N. FRANCHIMONT and HILMAR J. BACKER (*Rec. trav. chim.*, 1913, 32, 158—163. Compare T., 1912, 101, 2256).—The authors have examined the absorption spectra of aqueous solutions of the copper salts of methylnitroamine, ethylnitroamine, ethylnitrosohydroxylamine, of copper nitrate and ammoniacal copper nitrate at equivalent concentrations. The copper salts of the nitroamines are much more strongly absorbent than a solution of copper nitrate with the same copper content, whilst the light which is not absorbed is less violet than in the case of the copper salt of ethylnitrosohydroxylamine. The spectra of the copper salts of methyl- and ethyl-nitroamines are practically identical, and do not show an absorption band.

The electrical conductivity of solutions of the copper salts of nitroamines is noticeably less than that of their sodium salts or of ordinary copper salts. The copper salt of ethylnitrosohydroxylamine conducts still more feebly.

Solutions of the copper salts of nitroamines give the ordinary reactions for copper, whilst that of ethylnitrosohydroxylamine, although yielding precipitates with sodium hydroxide and with

hydrogen sulphide, gives only a brown coloration with potassium ferrocyanide.

The authors are led to the conclusion that the copper derivative of ethylnitrososulphohydroxylamine is probably a complex internal salt, but in view of the differences existing between this substance and the copper salts of the nitroamines, hesitate to assign a similar structure to the latter substances, although their intense colour and feeble electrical conductivity point to a relationship between the metal and nitrogen.

H. W.

Oxalyl Derivatives of Amino-acids. D. J. MEYERINGH (*Rec. trav. chim.*, 1913, 32, 140—157).—The author has prepared a series of oxalyl derivatives of amino-acids which contain the residues of two different amino-acids, by the action of ethyl chloroglyoxylate on the hydrochloride of the ester of an amino-acid, followed by treatment of the product so obtained with the potassium salt of a second amino-acid.

Ethyl chloroglyoxylate is best obtained by heating a mixture of equimolecular quantities of ethyl oxalate and phosphorus pentachloride until evolution of ethyl chloride ceases. It has b. p. 135°.

Methyl oxamidodiacetate, $C_2O_2(NH\cdot CH_2\cdot CO_2Me)_2$, has m. p. 158.5°, instead of 138—140° recorded by Kerp and Unger (*A.*, 1897, i, 269).

Oxamidoacetic acid, $NH_2\cdot CO\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, is obtained from oxamethane and potassium aminoacetate according to the method of Kerp and Unger (*loc. cit.*). The corresponding methyl ester, m. p. 157°, is obtained by treatment of the silver salt with an excess of methyl iodide and is converted by ammonia into the amide, needles, m. p. 251—252° (decomp.).

Ethyl ethoxalylaminoacetate, $CO_2Et\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$, b. p. 188°/18 mm., m. p. 16°, is prepared in 84% yield by heating an equimolecular mixture of ethoxalyl chloride and ethyl aminoacetate hydrochloride in dry benzene until evolution of hydrogen chloride ceases. It is converted by ammonia into the corresponding di-amide.

Methyl ethoxalyl- α -aminopropionate, $CO_2Et\cdot CO\cdot NH\cdot CHMe\cdot CO_2Me$, b. p. 173.5°/19 mm., is similarly prepared from ethyl chloroglyoxylate and methyl α -aminopropionate hydrochloride. The diamide, prepared by means of liquid ammonia, forms slender needles, m. p. 216.5°. No evidence of the formation of an isomeric diamide could be obtained.

Methyl glycineoxalyl- α -aminopropionate,

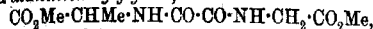
$CO_2H\cdot CH_2\cdot NH\cdot CO\cdot CO\cdot NH\cdot CHMe\cdot CO_2Me$, m. p. 136—137°, is prepared by the addition of methyl ethoxalyl- α -aminopropionate to a solution of potassium aminoacetate, care being taken that the temperature does not exceed 5°. At higher temperatures, and in the presence of excess of alkali, the ester is readily saponified, the corresponding acid decomposing at 210° when rapidly heated.

When a solution of α -alanine in potassium hydroxide is added to ethyl ethoxalylglycine, ethyl α -alanineoxalylglycine,

$CO_2H\cdot CHMe\cdot NH\cdot CO\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$, m. p. 142.5°, is obtained if the temperature does not rise above 5°. At higher temperatures, and in the presence of more concentrated potassium hydroxide, alanine separates and the potassium salt of ethyl

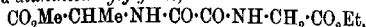
oxalylaminoacetate is produced. In alcoholic solution, alanine always separates to some extent, and the potassium salt of ethyl α -alanine-oxalylglycine is obtained.

Dimethyl α -alanineoxalylglycine,



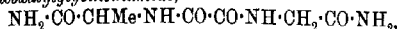
n. p. 98.5°, is prepared by saturating a methyl alcoholic solution of methyl glycine oxalyl- α -aminopropionate with hydrogen chloride.

Methyl ethyl α -alanineoxalylglycine,



n. p. 106°, is formed by similar treatment of a methyl alcoholic solution of ethyl α -alanineoxalylglycine or of an ethyl alcoholic solution of methyl glycineoxalyl- α -aminopropionate, whilst *diethyl α -alanine-oxalylglycine*, $\text{CO}_2\text{Et}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, m. p. 120°, is similarly produced from ethyl α -alanineoxalylglycine or from the corresponding free acid.

α -Alanineoxalylglycinediamide,



m. p. 272—274.5° (decomp.), is obtained by the action of liquid ammonia on dimethyl α -alanineoxalylglycine.

α -Aminoisobutyric acid does not react with ethyl ethoxalylglycine in the presence of the calculated quantity of potassium hydroxide at 0°.

Methyl ethoxalyl- α -phenylaminoacetate, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CO}_2\text{Me}$,

m. p. 56°, is prepared by heating ethyl chloroglyoxylate and methyl α -phenylaminoacetate hydrochloride in benzene solution. The corresponding *diamide* has m. p. 229°. By the action of oxalyl chloride (1 mol.) on methyl α -phenylaminoacetate hydrochloride in dry benzene, two isomeric forms of dimethyl oxalyl-di- $(\alpha$ -phenylaminoacetate), $\text{C}_6\text{H}_5(\text{NH}\cdot\text{CHPh}\cdot\text{CO}_2\text{Me})_2$, are obtained which may be separated by taking advantage of their different solubilities in benzene. They have m. p. 169—170° and 195° respectively.

Unsuccessful attempts have been made to prepare acetyl and nitro-derivatives of several of the above substances.

The presence of the oxalyl group has been actually ascertained in each of the above derivatives. They have further been examined with regard to their ability to give the biuret reaction. It appears that only those substances show this reaction in which at least one of the amino-groups is intact.

H. W.

Nitriles of Diaminodimethyl- and Diaminomethylethyl-succinic Acids and their Behaviour on Hydrolysis. OTTO DIELS and HAJIME OTSUKI (*Ber.*, 1913, 46, 1877—1883).—The cyanohydrins of dimethyl diketone and methyl ethyl diketone react with ammonia, yielding the nitriles of diaminodimethyl- and diaminomethylethyl-succinic acids which, on hydrolysis with hydrochloric acid, are converted into compounds $\text{C}_6\text{H}_8\text{N}_3\text{Cl}$ and $\text{C}_7\text{H}_{10}\text{N}_3\text{Cl}$ respectively. The constitution of the latter compounds has not been definitely established, but from their pronounced basic properties and their behaviour toward nitrous acid, the conclusion is drawn that they contain only one amino-group. The halogen atom is very firmly attached, and cannot be removed by any of the usual reagents.

When treated with nitric acid, the compounds are completely decomposed, yielding a chloro-nitromethane. The formation of the latter compound indicates that the halogen is attached to one of the carbon atoms.

Methyl ethyl diketone cyanohydrin, $\text{OH} \cdot \text{CMe}(\text{CN}) \cdot \text{CEt}(\text{CN}) \cdot \text{OH}$, is prepared by the action of hydrogen cyanide in ethereal solution on methyl ethyl diketone in the presence of potassium carbonate. It forms small, hygroscopic, crystalline plates, m. p. 76° , and when heated for five minutes with strong nitric acid is transformed into an *isomeride*, which sinters at 100° , m. p. 103° .

Diaminomethylethylsuccinonitrile, $\text{NH}_2 \cdot \text{CMe}(\text{CN}) \cdot \text{CEt}(\text{CN}) \cdot \text{NH}_2$, prepared by the action of concentrated aqueous ammonia on the preceding cyanohydrins at 0° , crystallises in hexagonal platelets or needles, m. p. 68° , and when maintained at 37° for two days with concentrated hydrochloric acid yields the compound, $\text{C}_7\text{H}_{10}\text{N}_4\text{Cl}$, which crystallises in lustrous, slender needles, m. p. 77.5° , forms a crystalline *hydrochloride* and *sulphate*, and on treatment with nitrous acid is converted into a *hydroxy*-compound, $\text{C}_7\text{H}_9\text{ON}_2\text{Cl}$, m. p. 147° .

s-Diaminodimethylsuccinonitrile, $\text{NH}_2 \cdot \text{CMe}(\text{CN}) \cdot \text{CMe}(\text{CN}) \cdot \text{NH}_2$, prepared from diacetylcyanohydrin (A., 1912, i, 942) and strong aqueous ammonia at 0° , crystallises in plates or leaflets, m. p. 166.5° . It is accompanied by a substance, $\text{C}_{12}\text{H}_{20}\text{O}_6\text{N}_6$, which forms small, tabular crystals, m. p. 234° (decomp.). On hydrolysis with concentrated hydrochloric acid at 37° , it yields the compound, $\text{C}_8\text{H}_{12}\text{N}_4\text{Cl}$. This forms long, lustrous needles, m. p. 140.5° , and is converted by the action of nitrous acid into a *hydroxy*-compound, $\text{C}_8\text{H}_{11}\text{ON}_2\text{Cl}$, which crystallises in lustrous needles, m. p. 227° , and when methylated by means of aqueous potassium hydroxide and methyl sulphate yields a *methyl ether*, $\text{C}_8\text{H}_{10}\text{ON}_2\text{Cl}$, crystallising in needles, m. p. 96° ; if the methylation is carried out with diazomethane, an isomeric *methyl ether* of m. p. $54-55^\circ$ is obtained.

F. B.

The Origin of Optically Active Compounds in the Living Cell; the Artificial Preparation of Optically Active Compounds Without the Intervention of Asymmetrical Molecules or Asymmetrical Forces. EMIL ERLÉNMEYER (*Biochem. Zeitsch.*, 1913, 52, 439-470).—In compounds of the type $\text{C}(\text{R}_1\text{R}_2\text{R}_3) \cdot \text{C}(\text{R}_4\text{R}_5\text{R}_6)$ there are, according to van't Hoff, twelve isomerides possible, of which eight can be derived from the four others, simply by rotation about the C—C axis. Isomerides which can be derived from one another simply by a rotation of this description are designated by the author as "relative isomerides" in contradistinction to the isomerides ("bond-isomerides") which can only be derived from one another by changes in the bonds uniting the R groups. If the assumption is made that mirror images have the same solubilities as one another, they are not separable from one another by fractional crystallisation. If, however, a racemic mixture containing the two mirror images can be subjected to such treatment that the antipodes can be converted into their "relative isomerides," then it is possible that the two constituents can change at different rates, or that the rotation about the C—C axis can take place in opposite directions. If, therefore, it is possible, by any

method, to produce "relative isomerides" in a racemic mixture, then it is also conceivable that a mixture can be produced which contains isomerides which are no longer mirror images of one another, and which are postulated to be separable from one another by a process of fractional crystallisation. The author in conjunction with G. Hilgen-dorff has applied the above conceptions to the investigation of the asparagines. He confirms the observations of Piutti, that a mixture of the *d*- and *l*-substances can be separated by crystallisation from hot water. He shows, furthermore, that a mixture, in equimolar proportions, of these two isomerides has double the solubility of either constituent separately, and that by recrystallisation at 20° the two constituents are not separable from one another. If, however, the mixture is first heated with water for some hours, subsequent fractional crystallisation can yield crops of crystals, which rotate light in the opposite direction. It is assumed here that, in accordance with the theory given above, the isomerides which form mirror images are converted into "relative isomerides" by the action of heat which are no longer mirror images. Copper salts were also obtained by fractional crystallisation from the mixture of the heated acids, of which the various fractions differed markedly from one another both in colour and solubilities. An attempt to obtain optically active isomerides in a similar way from racemic acid failed. It is pointed out, however, that when the *d*- and *l*-tartaric acids are combined there is development of heat, and a product of higher melting point, and less soluble in water than either the *d*- or *l*-acids, is obtained; in the case of combination of the *d*- and *l*-asparagines no heat is developed, and the product is more soluble than the antipodes and has a lower m. p. Apparently a true racemic combination is not produced in this case. The action of heat on the sodium-ammonium salt of racemic acid led, however, to a very partial separation into optically active isomerides. It is claimed that the experiments described above afford the first examples of the production of optically active substances without intervention of asymmetrical substances and forces, and the biological significance of the results is discussed in some detail.

S. B. S.

Preparation of Carbonyl Cyanide. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, 156, 1990—1992. Compare this vol., i, 715).—It has already been shown that, in a manner analogous to the combination with chlorine, hydrogen and ammonia producing carbonyl chloride, formaldehyde and formamide respectively, carbon monoxide undergoes combination with cyanogen if a mixture is exposed to ultra-violet light, yielding carbonyl cyanide, $\text{CN}\cdot\text{CO}\cdot\text{CN}$.

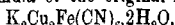
Endeavours to prepare this substance by other methods reveal the fact that the silent electric discharge, which, although it frequently causes similar effects to ultra-violet light, exerts a quite distinct effect in other cases, also gives rise to a combination of the two gases. The mixture may contain varying proportions of the gases as long as neither becomes exhausted, but the action is most rapid when equal volumes are applied. With a tension of 6000 volts combination occurs much more rapidly than in ultra-violet light, and in one experiment

a mixture of 5 c.c. of carbon monoxide with an approximately equal volume of cyanogen gave a contraction of 3 c.c. in ten minutes. The yellow solid product is partly soluble in water and wholly soluble in alkalis. From the slow rate of its hydrolysis by dilute sulphuric acid, the substance evidently represents an even higher stage in the polymerisation of the simple molecule $\text{CN}\cdot\text{CO}\cdot\text{CN}$ than the product of ultra-violet illumination.

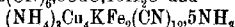
Attempts were made to prepare the unpolymerised substance by chemical processes, such as the action of carbonyl chloride on cyanide of silver or mercury, or from carbon monoxide and cyanogen by mere heating, but the results were consistently negative.

D. F. T.

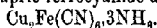
Some Complex Copper Alkali Ferrocyanides. KSHITIBHUSAN BHADURI and SARASHILAL SARKAR (*Zeitsch. anorg. Chem.*, 1913, 82, 164—172).—Dextrose is added to a solution of potassium ferrocyanide, which is then mixed with Fehling's solution. A cream-coloured precipitate is obtained, which is crystalline if the solutions are dilute. It is washed with boiling water and dried in a vacuum over sulphuric acid. It becomes violet and blue with sulphuric acid, and yields a nitroprusside with nitric acid. The crystalline characters are described. The formula of the original salt is



the blue salt being $\text{K}_2\text{Cu}_2\text{Fe}(\text{CN})_6\cdot\text{K}_2\text{Cu}_2[\text{Fe}(\text{CN})_6]_2$, and the nitroprusside, $\text{K}_2\text{Fe}(\text{CN})_5\cdot\text{NO}\cdot 2\text{Cu}_2\text{Fe}(\text{CN})_5\cdot\text{NO}\cdot 13\text{H}_2\text{O}$. Alkali yields a compound $\text{K}_2\text{CuFe}(\text{CN})_6\cdot\text{CuO}\cdot 3\frac{1}{2}\text{H}_2\text{O}$. *Lithium copper ferrocyanide*, $\text{Li}_2\text{Cu}_2\text{Fe}(\text{CN})_6\cdot 4\text{H}_2\text{O}$, is lemon-yellow, and the sodium compound has also been obtained. The ammonium salt is obtained by dissolving cupric oxide in ammonia; and adding dextrose and ammonium ferrocyanide, giving a red precipitate, $(\text{NH}_4)_2\text{Cu}_2\text{Fe}(\text{CN})_6\cdot 3\text{NH}_3$, and, from the filtrate, pale blue crystals of $(\text{NH}_4)_2\text{Cu}_2[\text{Fe}(\text{CN})_6]_2\cdot 8\text{NH}_3$. The compounds $2\text{CuK}_2\text{Fe}(\text{CN})_6\cdot 8\text{CuO}\cdot 16\text{H}_2\text{O}$ and



have also been obtained. When copper sulphate is added to potassium ferrocyanide and the precipitate is dissolved in ammonia, brown crystals of ammoniacal cupric ferrocyanide are obtained,



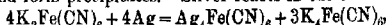
The nature of the reduction process is unknown.

C. H. D.

The Action of Different Metals on Potassium Ferri- and Ferricyanide Solutions. GEORGE MCPHAIL SMITH [and RALPH ATKINSON LINDH] (*Zeitsch. anorg. Chem.*, 1913, 82, 63—70. Compare Beutel, A., 1912, i, 543).—Powdered iron prepared by reduction reduces potassium ferri- and ferricyanide in an atmosphere of hydrogen:



Nickel and zinc also reduce to ferrocyanide without passing into solution, and form precipitates. Silver reacts in the cold:



but at 100° silver goes into solution as a complex salt. With mercury, metallic iron is first formed: $2\text{K}_3\text{Fe}(\text{CN})_6 + 3\text{Hg} = 3\text{K}_2\text{Hg}(\text{CN})_4 + 2\text{Fe}$. This iron then reacts as above, and, in presence of alkali hydroxide,

ferric hydroxide is ultimately formed. Gold dissolves slowly in ferriocyanide solutions.

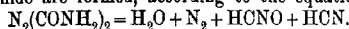
[With MICHELE CROCE*]—Silver ferrocyanide dissolves in potassium ferrocyanide solution, forming potassium silver cyanide, $KAg(CN)_2$.

C. H. D.

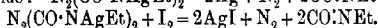
Univalent Nickel Compounds. II. ITALO BELLUCCI and R. CORELLI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 703—708. Compare this vol., ii, 604).—Continuing their work on the nature of the compound contained in the red liquid obtained by the reduction of potassium nickelocyanide, the authors criticise adversely the second also of the analytical methods employed by Moore (*loc. cit.*), so that they reject the formula Ni_3X_2 proposed by that author. By three analytical methods they obtain concordant results indicating that the red solution contains a cyano-salt in which nickel is univalent. The analytical methods employed were: (1) the measurement of the amount of hydrogen evolved by the solution in the warm; (2) titration with $N/10$ iodine solution; (3) titration with a standard hydrogen peroxide solution.

R. V. S.

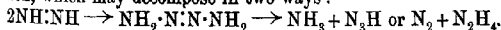
New Compounds and Scissions of Azodicarboxylic Acid. OTTO DIEHL and MAX PAQUIN (*Ber.*, 1913, 46, 2000—2013).—The decomposition of derivatives of azodicarboxylic acid on dehydration, hydrolysis or heating is described. When azodicarboxylamide is heated with phosphoric oxide, nitrogen, water, cyanic acid and hydrogen cyanide are formed, according to the equation:



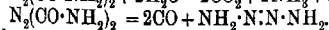
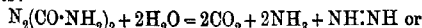
Substituted azoamides, such as azodicarboxydiethylamide, yield isocyanates and isonitriles: $N_2(CO \cdot NHEt)_2 = H_2O + N_2 + C_2H_5NCO + C_2H_5NC$. The same compound also readily forms a brick-red silver salt which decomposes at 144° , or when treated with iodine, into ethylcarbimide: $N_2(CO \cdot NAgEt)_2 = 2Ag + N_2 + 2CO \cdot NEt$;



When azodicarboxylamide is heated with concentrated sulphuric acid, it decomposes into carbon dioxide, carbon monoxide, sulphur dioxide and nitrogen, but, in the cold, hydrazine sulphate and hydrazoic acid are formed. When boiled with dilute sulphuric acid, the compound gives a larger yield of hydrazoic acid, the other products including carbon monoxide, carbon dioxide, nitrogen and hydrazine and ammonium sulphates. Angeli (A., 1910, ii, 844) observed the production of hydrazoic acid under these conditions from azodicarboxylic acid itself, and explained it by assuming that di-imine, $NH:NH$, is first formed, and that it polymerises to the hypothetical tetrazen, which may decompose in two ways:



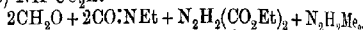
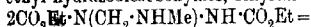
The primary decomposition of azodicarboxylamide might also follow two courses:



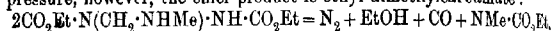
Methyl hydrazodicarboxylate, $N_2H_2(CO_2Me)_2$, was obtained in radiating bundles of broad needles by the action of methyl chloroformate on

hydrazine hydrate, and oxidised by concentrated nitric acid to *methyl azodicarboxylate*. The latter has b. p. $85^{\circ}/7$ mm., is hydrolysed by water to the hydrazo-ester, carbon dioxide and hydrazoic acid, and is oxidised by fuming nitric acid to oxalic acid.

Whereas primary amines convert the esters of azodicarboxylic acid into amides, secondary and tertiary amines usually form additive compounds which, on hydrolysis with dilute acids, yield the corresponding hydrazo-esters together with aldehydes and amines which contain one radicle less attached to the nitrogen atom than the original amine does. Thus the compound of ethyl azodicarboxylate with dimethylamine yields ethyl hydrazodicarboxylate, formaldehyde and methylamine, its constitution being therefore represented by the formula $\text{CO}_2\text{Et}\cdot\text{N}(\text{CH}_2\cdot\text{NHMe})\cdot\text{NH}\cdot\text{CO}_2\text{Et}$. The compound forms well-defined prisms or rhombic plates, m. p. 95° , decomposes, when the aqueous solution is boiled, into ethyl hydrazodicarboxylate, dimethylamine, nitrogen and carbon dioxide, and is oxidised by nitric acid to ethyl azodicarboxylate. When submitted to dry distillation, it decomposes vigorously, giving a good yield of hydrazomethane, together with ethyl hydrazodicarboxylate, ethylcarbimide and formaldehyde:



When the decomposition and distillation are carried out under reduced pressure, however, the chief product is ethyl dimethylcarbamate:



The latter was characterised by conversion into methylnitroamine (Franchimont and Klobbie, A., 1889, 492).

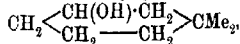
The compound, $\text{CO}_2\text{Et}\cdot\text{N}(\text{CHMe}\cdot\text{NHEt})\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, prepared by mixing ethyl azodicarboxylate with diethylamine, forms clusters of needles, m. p. 68° , is sparingly soluble in cold water or water at 80 – 90° , but is readily soluble at 50° , and yields acetaldehyde on hydrolysis. The compound, $\text{CO}_2\text{Me}\cdot\text{N}(\text{CH}_2\cdot\text{NMePh})\cdot\text{NH}\cdot\text{CO}_2\text{Me}$, obtained from methyl azodicarboxylate and dimethylaniline, crystallises from ether in prismatic columns and rhombic plates, m. p. 95 – 96° , and yields formaldehyde, methylaniline, and methyl hydrazodicarboxylate on hydrolysis. The compound,



prepared by mixing azodicarboxylethylamide with ether and dimethylamine in the cold in a sealed tube, forms rhombic plates, m. p. 109 – 111° (decomp.), and yields formaldehyde on hydrolysis.

J. C. W.

1:1-Dimethylcyclohexane. NICOLAI D. ZELINSKI and NICOLAI N. LEPESCHKIN (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 613–616).— β -Methyl- Δ^2 -hepten-2-one was converted into the η -acetyl derivative, the latter transformed by the action of sulphuric acid into 6-acetyl-1:1-dimethylcyclohexan-5-one, and this hydrolysed to 1:1-dimethylcyclohexan-5-one, which, on reduction in ethereal solution by means of sodium and water, gave 1:1-dimethylcyclohexan-5-ol,



b. p. $185^{\circ}/754$ mm., D_4^{25} 0.9071, n_D^{25} 1.4558. Reduction of the

alcohol with hydriodic acid yields 1:1-dimethylcyclohexane, b. p. 119.2—119.7°, D_4^{20} 0.7843, D_4^{25} 0.7792, n_D^{20} 1.4320 (compare Crossley and Renouf, T., 1905, 87, 1487). When treated with bromine in presence of aluminium bromide, this hydrocarbon is readily converted into tetrabromo-*p*-xylene, one of the methyl groups migrating to the para-position under the conditions of bromination (compare A., 1902, i, 143). T. H. P.

The Benzene Problem. KURT GEBHARD (*J. pr. Chem.*, 1913, [ii], 88, 94—96).—A reply to Liebig (this vol. i, 607). F. B.

A New Method for the Introduction of Iodine into Aromatic Substances. KARL ELBS and A. JAROSLAVZEV (*J. pr. Chem.*, 1913, [ii], 88, 92—94).—Iodo-derivatives of aromatic hydrocarbons may be readily prepared by boiling the latter with iodine and sodium persulphate in glacial acetic acid solution. Thus benzene yields iodo- and *p*-diiodobenzene, whilst toluene gives rise to *o*- and *p*-iodotoluenes.

The following iodo-compounds have also been prepared by this method: 4-iodo-*m*-xylene, 4-iodo-*o*-xylene, 2-iodo-*p*-xylene, and iodo-*ψ*-cumene.

s-Di-*p*-iododiphenylethane, prepared from dibenzyl, has m. p. 152°; the position of the iodine atoms has been established by its oxidation to *p*-iodobenzoic acid by chromic acid in glacial acetic acid solution.

F. B.

Some Aromatic Fluorine Compounds. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1913, 241—278).—The compounds described are mostly prepared by decomposing aromatic diazonium salts with hydrofluoric acid in vessels of silver or platinum. They were obtained for thermochemical investigations (compare A., 1907, ii, 9; 1908, ii, 354; 1909, ii, 297).

o-Fluoronitrobenzene could not be prepared: the para-isomeride forms colourless crystals, m. p. 27°, b. p. 205°/735 mm., and the *meta*-derivative has m. p. 3.6°, b. p. 200°/756 mm., D_{17} 1.3272, n_D^{20} 1.5207.

1-Fluoro-2:4-dinitrobenzene forms large, colourless, hard crystals m. p. 25.8°, b. p. 178°/25 mm.

m-Fluoroacetanilide crystallises in large, colourless prisms, m. p. 84.5°; the para-isomeride forms tiny needles, m. p. 152°. 4-Fluoro-3-nitroacetanilide separates in very pale yellow needles, m. p. 138.5°.

p-Fluorophenol, prepared by heating fluorophenetole with aluminium chloride, has b. p. 185.5°. It forms transparent, tabular crystals, m. p. 26.5—27°, but this modification changes on keeping into a stable form, m. p. 45°, consisting of acicular crystals resembling phenol.

m-Fluorophenol, prepared by decomposing *m*-fluorobenzenediazonium sulphate, forms large, prismatic crystals, m. p. 13.7°. *o*-Fluorophenol, b. p. 151—152°, m. p. 16.1°, has a penetrating odour.

ω-Trifluoro-*m*-cresol, $CF_3 \cdot C_6H_4 \cdot OH$, prepared by diazotising trifluorotoluidinesulphate and decomposing the diazonium compound with

dilute sulphuric acid, forms a viscid liquid, b. p. 178.3°, which yields crystals, m. p. -1.8°.

On diazotising *o*-phenetidine in hydrofluoric acid a mixture of *o*-fluorophenetole and ordinary phenetole is obtained. *o*-Fluorophenetole has b. p. 171.4°, m. p. -16.7°. *m*-Fluorophenetole, prepared in a similar manner, is a colourless liquid, b. p. 171.4°/755 mm., D_{18}^{20} 1.0716, n_D^{20} 1.4847.

p-Fluorophenetole cannot be separated from phenetole by distillation; after fractional crystallisation the pure product had m. p. -8.5°, b. p. 172.8°/766 mm., D_{18}^{20} 1.07148, n_D^{20} 1.48257. The product described by Valentiner and Schwarz (*Zeitsch. angew. Chem.*, 1898, 11, 441), b. p. 197°, as *p*-fluorophenetole is shown to be mainly *p*-chlorophenetole.

On nitration of *p*-fluorophenol, 4-fluoro-2-nitrophenol is obtained, crystallising in hexagonal prisms, m. p. 73.7°; the sodium and potassium salts form long, red needles which explode when heated.

The corresponding 4-fluoro-2-nitrophenetole yields colourless crystals, m. p. 33.7°. 4-Fluoro-2:6-dinitrophenol crystallises in very beautiful yellow prisms, m. p. 50.2°.

On nitration of *m*-fluorophenol, a dinitro-derivative is obtained in large, colourless, straw-like crystals becoming yellow on exposure to light, m. p. 72—74°; the constitution has not been established.

p-Difluorobenzene prepared from *p*-fluoroaniline is an oil, b. p. 88—89°, D_{18}^{20} 1.1725, n_D^{20} 1.4422, m. p. -23.7°.

On nitration 1:4-difluoro-2-nitrobenzene is obtained as a pale yellow oil, b. p. 103°/25 mm., m. p. -11.7°; it is very viscous at low temperatures. The oil has D_{17}^{20} 1.4671, n_D^{20} 1.6115. E. F. A.

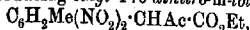
Chloronitrotoluenes with Reactive Chlorine. WALTHER BORSCHÉ and ANNA FIEDLER (*Ber.*, 1913, 46, 2117—2131. Compare A., i, 175).—In continuation of the earlier investigation which led to the isolation of pure 2-chloro-3:5-dinitrotoluene, the authors have turned their attention to the corresponding derivatives of *p*- and *m*-chlorotoluenes. Their results indicate, among other facts, that pure 4-chloro-3:5-dinitrotoluene has not been previously obtained (compare Höning, A., 1887, 1034).

The further nitration of 4-chloro-3-nitrotoluene by gradual addition to a cooled mixture of equal volumes of sulphuric acid and nitric acid (D 1.52) gives an impure reaction product from which by repeated crystallisation from alcohol pure 4-chloro-3:5-dinitrotoluene, needles, m. p. 115—116°, can be separated. It reacts with ethyl sodiomalonate in warm ethereal solution, producing, after acidification, ethyl 2:6-dinitro-*p*-tolylmalonate, $C_6H_4Me(NO_2)_2 \cdot CH(CO_2Et)_2$, colourless crystals, m. p. 90°, which on heating with a mixture of acetic acid and a little diluted sulphuric acid passes into 2:6-dinitro-*p*-tolylacetic acid,

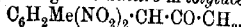
$C_6H_4Me(NO_2)_2 \cdot CH_2 \cdot CO_2H$, colourless needles, m. p. 241—242° (decomp.). 4-Chloro-3:5-dinitrotoluene also reacts with aniline, yielding 3:5-dinitro-4-anilinotoluene. The chlorodinitrotoluene can also be obtained in small quantity by the action of toluene-*p*-sulphonyl chloride on dinitro-*p*-cresol in the presence of diethylaniline. In preparing the compound by the first method a

substance, m. p. 108°, possibly 4-chloro-2:5-dinitrotoluene, which does not react with aniline, is simultaneously produced.

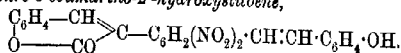
The main product in the nitration of *m*-chlorotoluene by Reverdin and Crepieux's method (A., 1900, i, 638) is 3-chloro-4:6-dinitrotoluene, m. p. 91°. It reacts in warm ethereal solution with ethyl sodioacetoacetate, producing *ethyl 4:6-dinitro-m-tolylacetoacetate*,



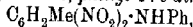
yellow tablets, m. p. 98°, which on warming with sulphuric acid undergoes scission, yielding *4:6-dinitro-m-tolylacetone*,



leaflets, m. p. 92°; also with ethyl sodiomalonate, it gives *ethyl 4:6-dinitro-m-tolylmalonate*, pale yellow crystals, m. p. 62°, which on heating with diluted sulphuric acid in acetic acid solution passes into *4:6-dinitro-m-tolylacetic acid*, colourless needles, m. p. 176°; this substance when maintained at its m. p. loses carbon dioxide with production of *4:6-dinitro-1:3-xylene*, m. p. 93–94°. *Ethyl 4:6-dinitro-m-tolylacetate*, colourless needles, m. p. 70°, is slowly converted by the action of sodium and more *m*-chlorodinitrotoluene in alcoholic solution at the ordinary temperature into *ethyl 4:6:4':6'-tetranitro-di-m-tolylacetate*, $\text{CO}_2\text{Et} \cdot \text{CH}_2[\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2]_2$, needles, m. p. 159–160°, and also condenses at 180° with salicylaldehyde in the presence of a little piperidine, producing *3-o'-p-dinitro-m-tolylcoumarin*, $\text{C}_6\text{H}_4-\text{CH} \begin{array}{c} \nearrow \\ \text{O} \end{array} \text{CO} \begin{array}{c} \searrow \\ \text{O} \end{array} \text{C}-\text{C}_6\text{H}_2\text{Me}(\text{NO}_2)_2$, yellow needles, m. p. 240°, with a little *4:6-dinitro-3-coumarino-2'-hydroxystilbene*,

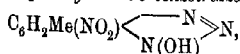


4:C-Dinitro-m-toluidine is obtainable by heating the corresponding chlorodinitrotoluene with alcoholic ammonia at 100°, and if the ammonia be replaced by aniline, *phenyl 4:6-dinitro-m-tolylamine*,



orange-coloured leaflets, m. p. 145°, is obtained. The former of these products readily condenses at 180–190° with benzaldehyde in the presence of piperidine with formation of *4:6-dinitro-3-anilinostilbene*, $\text{NHPh} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{CH} : \text{CHPh}$, deep red leaflets, m. p. 182°. The chlorodinitrotoluene likewise condenses with piperidine when heated with the hydrochloride of the base and sodium acetate in alcoholic solution, giving *4:6-dinitro-3-piperidinotoluene*, yellow rhombs, m. p. 116°; this can be further condensed with benzaldehyde, *4:6-dinitro-3-piperidinostilbene*, yellowish-red crystals, m. p. 172°, being produced.

If the mother liquors from the crystallisation of 3-chloro-4:6-dinitrotoluene are treated with ethyl sodiomalonate or sodioacetoacetate, an unreactive isomeride, *3-chloro-2:4-dinitrotoluene*, yellowish-white needles, m. p. 73°, remains unaffected; its structure is indicated by its conversion through the corresponding *dinitrotolylhydrazins (hydrochloride, yellow needles)* by the action of ammonium hydroxide into *4-nitro-5-methyl-1-hydroxy-1:2:3-benzotriazole*,



incomp. at 176° (compare Borsche and Rantschew, A., 1911, i, 329).]

2-Chloro-3:5-dinitrotoluene reacts with ethyl sodioacetacetate in ethereal suspension with formation of *ethyl 4:6-dinitro-o-tolylacetate*, yellow needles, m. p. 79—80°, from which *4:6-dinitro-o-tolylacetone*, pale yellow leaflets, m. p. 103—104°, can be obtained by hydrolysis with diluted sulphuric acid. In a similar manner, condensation with ethyl sodiomalonate yields *ethyl 4:6-dinitro-o-tolylmalonate*, yellow prisms, m. p. 87—88°, which on heating with diluted sulphuric acid in acetic acid solution is converted into *4:6-dinitro-o-tolylacetic acid*, colourless needles, m. p. 202° (decomp.); this when heated readily loses a molecule of carbon dioxide with formation of *3:5-dinitro-1:2-xylene*, m. p. 74—75°. D. F. T.

Solubilities of the Rare Earth Salts of Bromonitrobenzene-sulphonic Acid. S. H. KATZ and CHARLES JAMES (*J. Amer. Chem. Soc.*, 1913, 35, 872—874).—1:4:2-Bromonitrobenzenesulphonic acid, prepared by sulphonation of bromonitrobenzene, forms nicely crystalline salts with lanthanum (8H₂O), cerium (8H₂O), yttrium (10H₂O), praseodymium (8H₂O), neodymium (8H₂O), samarium (10H₂O), europium (10H₂O), gadolinium (10H₂O), erbium (12H₂O), thulium (12H₂O), and ytterbium (12H₂O). The solubility of each salt was determined at 25°, and it is interesting that on plotting the solubilities against the atomic weight, salts containing the same amount of water of crystallisation fall on distinct portions of the curve. D. F. T.

Nitration of Iodobenzene. ARNOLD F. HOLLEMAN (*Rec. Trav. chim.*, 1913, 32, 134—139).—In a previous investigation of the nitration of iodobenzene (A., 1912, i, 87), the author has found that the quantity of ortho-isomeride formed is less than that obtained in the nitration of bromobenzene, whilst in the nitration of other aryl haloids, the quantity of this isomeride increases with the atomic weight of the halogen, and also that a greater amount of *o*-iodonitrobenzene is obtained at -30° than at 0°, although the amount of accessory product generally increases with increasing temperature of nitration.

[With A. F. H. LOBBY DE BRUYN and W. J. DE MOOR.]—The previous work has been repeated and a new source of error discovered due to the ready solubility of *o*-iodonitrobenzene in iodobenzene, in which *p*-iodonitrobenzene is practically insoluble. The iodobenzene is now added slowly to the nitric acid (D 1.482 for nitration at 0° and D 1.488 for nitration at -30°) with brisk stirring, smaller quantities of concentrated nitric acid being added from time to time if the mass becomes too viscous. Agitation is continued for two to three hours after completion of the addition of iodobenzene. The mass is then poured into water, filtered, dried, and distilled under diminished pressure. In this manner the determination of the point of solidification is greatly facilitated.

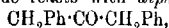
The authors are led to the conclusion that the iodobenzene does not differ from that of the other phenyl haloids. At -30°, 39.1% of the ortho- and 60.9% of the para-isomeride are obtained, whilst at 0° the figures are 41.1% ortho- and 58.7% para-isomeride. H. W.

Some Diphenylpentanes and the Corresponding Dicyclohexylpentanes. PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1913, 156, 1951—1954. Compare this vol., i, 716; A., 1912, i, 617, 757).—The authors have already reduced various diphenylethanes, diphenylpropanes, and diphenylbutanes to the corresponding dicyclohexyl derivatives, and in order to test the general character of the hydrogenation still further, have now submitted three of the eighteen theoretically possible diphenylpentanes to similar treatment.

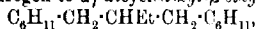
By catalytic treatment of β -phenylpropionic acid with thorium or iron oxide, *ae*-diphenylpentan- γ -one, $\text{CH}_3\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, was first prepared, which, by contact with a not too active nickel at 180° in the presence of hydrogen, is converted smoothly into *ae*-diphenylpentane, a fluorescent colourless liquid, b. p. 321° (corr.), D_4^{20} 0.9924, n_D^{20} 1.559. By hydrogenation under the influence of a very active nickel at 165° , this hydrocarbon is entirely reduced to *ae*-dicyclohexylpentane, $\text{C}_6\text{H}_{11}\cdot[\text{CH}_2]_3\cdot\text{C}_6\text{H}_{11}$, a colourless liquid, b. p. 311° (corr.), D_4^{20} 0.8832, n_D^{20} 1.479, which resists the action of a cold mixture of nitric and sulphuric acids.

Methyl isovalerate reacts with magnesium phenyl bromide, yielding *ae*-diphenyl- γ -methylbutanol, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$, which undergoes dehydration when distilled under the ordinary pressure, with production of *ae*-diphenyl- γ -methyl- Δ^4 -butene, $\text{CHMe}_2\cdot\text{CH}\cdot\text{CPh}_2$, a pale yellow liquid, b. p. 298 — 299° (corr.), D_4^{20} 0.9792, n_D^{20} 1.581. When submitted to the action of hydrogen under the influence of a sluggish nickel catalyst at 180° , the last-named hydrocarbon undergoes reduction to *ae*-diphenyl- γ -methylbutane, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CHPh}_2$, a colourless, slightly fluorescent liquid, b. p. 297° (corr.), D_4^{20} 0.9756, n_D^{20} 1.551, which is still further reduced under the catalytic influence of a very active specimen of nickel at 160 — 165° , giving *ae*-dicyclohexyl- γ -methylbutane, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{C}_6\text{H}_{11})_2$, a colourless liquid, b. p. 290 — 291° (corr.), D_4^{20} 0.9058, n_D^{20} 1.489.

Magnesium ethyl iodide reacts with diphenylpropanone,



which is obtainable by catalytic treatment of phenylacetic acid with iron oxide, producing dibenzylethylcarbinol, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{OH})(\text{CH}_2\text{Ph})$; this passes on mere distillation under ordinary pressure into α -diphenyl- β -ethyl- Δ^4 -propylene, $\text{CHPh}\cdot\text{C}(\text{Et})\cdot\text{CH}_2\text{Ph}$, b. p. 306 — 307° , D_4^{20} 1.0159, n_D^{20} 1.589. By means of a sluggish nickel catalyst at 230° this can be hydrogenated to α -diphenyl β -ethylpropane, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{Et})\cdot\text{CH}_2\text{Ph}$, a colourless, fluorescent liquid, b. p. 304 — 305° (corr.), D_4^{20} 0.9855, n_D^{20} 1.553. When submitted to an active nickel catalyst below 180° it is reduced by hydrogen to α -dicyclohexyl- β -ethylpropane,



a colourless liquid, b. p. 296° (corr.), D_4^{20} 0.8966, n_D^{20} 1.843, which is not attacked by a cold mixture of sulphuric and nitric acids.

A comparison of the m. p.'s and b. p.'s of the diphenyl derivatives in which the two phenyl groups are connected by a normal chain of carbon atoms reveals the fact that whilst the latter increases steadily with an increasing number of linking atoms, the m. p.'s exhibit an undulating increase similar to that observed with the dicarboxylic acids. It is also noteworthy that whilst all the diphenyl hydro-

carbons are fluorescent, this property is most marked in those having the two phenyl radicles coupled by a normal chain of methylene linkings; the *dicyclohexyl* derivatives possess no fluorescence.

D. F. T.

The Constitution of Naphthalene. EUGEN BAMBERGER (*Ber.*, 1913, 46, 1899—1903).—Since his earlier publications (a list of which is appended to the paper), the author's views on this subject have undergone modifications. Although he still regards the symmetry of naphthalene as highly probable, he realises that there has been no final proof. The formula suggested by Willstätter and Waser (*A.*, 1912, i, 17) fails to express the reduction of naphthalene and its derivatives, which possess no true aromatic character, to aromatic compounds. This peculiar behaviour of naphthalene derivatives can be explained by other symmetrical formulæ in addition to the author's, provided that they do not include a true benzene ring, but the author repeats his earlier statement (*J. pr. Chem.*, 1890, 42, [2], 205) that it is not possible to represent completely the various chemical phenomena presented by naphthalene derivatives in any one formula of the usual type.

D. F. T.

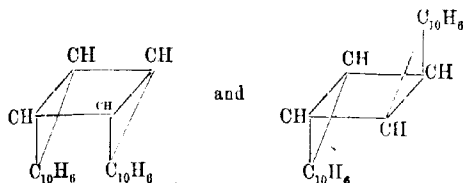
10-Bromophenanthrene-3- or -6-sulphonic Acid. HÅKAN SANDQVIST (*Annalen*, 1913, 398, 125—137).—By heating with 96—97% sulphuric acid on the water-bath and finally at 150—155°, 10-bromophenanthrene is converted into an acid which is proved to be 10-bromophenanthrene-3- or -6-sulphonic acid, and is isolated as the potassium salt. The free acid, prepared from the chloride and water at 130—135°, is an almost colourless, crystalline powder. It contains 3H₂O, and has m. p. 162—164·5° (anhydrous, 200—201·5°). A 10% aqueous solution of the acid, which is as clear and viscous as water, becomes syrupy by the addition of a little dilute hydrochloric, nitric, or sulphuric acid, and finally deposits crystals of the acid by further addition of the mineral acid. The following salts are described, the figures in brackets denoting the weight of anhydrous salt dissolved by 100 grams of water at 19·5°: *ammonium* salt containing H₂O (0·327), *sodium* salt containing 1½H₂O (0·142), *potassium* salt with H₂O (0·163), *calcium* salt with 4H₂O, *barium* salt with 2½H₂O, *cupric* salt with 4H₂O; the last three salts are quantitatively insoluble. The *methyl* ester, m. p. 172·5—173°, *ethyl* ester, m. p. 173—173·3°, *chloride*, C₁₄H₉O₂ClBrS, m. p. 184·5—185°, *sulphonamide*, m. p. 280—281°, and dimorphous *anilide*, m. p. 185·5—186° or 193°, are described.

By oxidation with chromic acid in boiling glacial acetic acid, 10-bromophenanthrene-3-(or 6)-sulphonyl chloride and methyl 10-bromophenanthrene-3-(or 6)-sulphonate respectively yield substances, m. p. 230—238° and 230—233°, which are apparently phenanthraquinone-3-sulphonyl chloride, m. p. 232—234°, and methyl phenanthraquinone-3-sulphonate, m. p. 234°, respectively.

Potassium or methyl 10-bromophenanthrene-3-(or 6)-sulphonate are not attacked by reducing agents in acid or neutral media; concentrated aqueous ammonia and zinc dust on the water-bath reduce the potassium salt, yielding phenanthrene-3-sulphonic acid.

C. S.

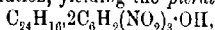
Photochemical Transformations of Acenaphthylene. II.
 KARL DZIEWONSKI and C. PASCHALSKI (*Ber.*, 1913, **46**, 1986—1992.
 Compare A., 1912, i, 844).—The two hydrocarbons, m. p. 306—307°
 and m. p. 232—234°, which are obtained by the action of sunlight on
 acenaphthylene are *cis-trans*-isomerides and may be represented by
 the formulæ :



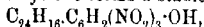
The compounds are formed in different quantities according to the nature and concentration of the solution and to the intensity of the light. They both yield naphthalic anhydride on oxidation and are partly converted into the parent substance in the molten state, but they form entirely different picrates and bromo compounds. Although it cannot be said which of the isomerides is the labile modification, it is proposed to call the higher and the lower melting forms α - and β -heptacyclene respectively.

The former is the chief product when a benzene solution of acenaphthylene is illuminated, but the β -form predominates when petroleum is used as the solvent. β -Heptacyclene, $C_{24}H_{18}$, forms large, monoclinic prisms or tablets, $\alpha : b : c = 0.7223 : 1 : 0.9527$, $\beta = 119^\circ 8'$, and is readily soluble in benzene. Both substances yield new, complex hydrocarbons when kept in the molten state for some time, but, when the mass is quickly cooled, some acenaphthylene is obtained and this is probably the parent of the new compounds, for it is unstable above 110° .

α -Heptacyclene combines with two molecules of picric acid in ethylene dibromide solution, yielding the *picrate*,



in orange needles, m. p. $225-227^\circ$, which are decomposed even by solvents, whereas β -heptacyclene forms a stable *picrate*,



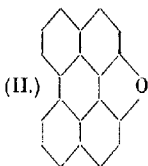
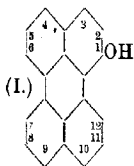
in carmine-red needles, m. p. $215-216^\circ$. The α -hydrocarbon reacts very sluggishly with bromine in the cold, but the β -form absorbs bromine at once.

J. C. W.

Perylene and Its Derivatives. II. RICHARD WEITZENBÖCK and CHRISTIAN SEER [with A. VON BARTSCH] (*Ber.*, 1913, **46**, 1994—2000. Compare A., 1910, i, 616).—Attempts have been made to improve the yield of perylene or its derivatives. The best result was obtained by the condensation of 4:4'-dicyano-1:1'-dinaphthyl to 3:10-dicyanoperylene.

From bromonaphthalene and aluminium chloride, a 4% yield of perylene was obtained at 140° , but at $30-35^\circ$ the product was 2:2'-dinaphthyl, which was probably formed by the rearrangement of 1:1'-dinaphthyl. β -Dinaphthylene oxide (Eckstein, A., 1905, i, 885)

was also heated with aluminium chloride, when alkali extracted from the product, 1-hydroxyperylene (I). This forms long, slender, yellow needles, m. p. 197°, which give yellow solutions with green fluorescence, and yield a benzoate, $C_{27}H_{16}O_2$, in slender, lemon-yellow needles, m. p. 170–170.5°, and a methyl ether in yellow nodules, m. p. 111°. The residue from the extraction with alkali contained 1:12-furoperylene (II), which forms a reddish-brown powder, and gives dark red solutions with yellowish-brown fluorescence.



3:10-Dicyanoperylene, $C_{22}H_{10}N_2$, was obtained in good yield by the condensation of 4:4'-dicyano-1:1'-dinaphthyl (Seer and Scholl, this vol., i, 734) in brown, microscopic needles, m. p. 368–369°. It is sparingly soluble in acetic acid or xylene with intense green fluorescence, and yields 3:10-perylenedicarboxylic acid, $C_{22}H_{12}O_4$, when heated with alcoholic sodium hydroxide in a sealed tube. The acid forms reddish-brown, microscopic needles, and the solutions in alkalis are yellow with intense green fluorescence. The ethyl ester, $C_{26}H_{20}O_4$, forms brick-red leaflets, m. p. 247–248°.

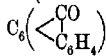
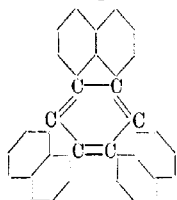
4:4'-Di-iodo-1:1'-dinaphthyl (Willgerodt and Schlösser, A., 1900, i, 282) was prepared from naphthidine by treating the diazonium salt with potassium iodide. When heated with aluminium chloride, extensive decomposition took place.

J. C. W.

Degradation of Decacycene [Trinaphthylenebenzene]. KARL DZIEWOŃSKI [with J. PODGÓRSKA and A. MIKŁASZEWSKI] (Ber., 1913, 46, 2156–2162).—When finely powdered decacycene (A., 1903, i, 431) is heated for some hours with sodium dichromate and 30% sulphuric acid, it is broken down into tribenzoylenebenzenetricar-

boxylic acid, $C_6(\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_3 \cdot \text{CO}_2\text{H} \end{smallmatrix})_3$, which is formed in good quantity, as a brownish-red, voluminous, microcrystalline mass, m. p. above 360°.

The acid gives blood-red solutions in alkalis, and forms, by precipitation, a brown silver salt, $C_{30}H_{18}O_6Ag_3$, and a reddish-brown barium salt, $(C_{30}H_{18}O_6)_2Ba_2$. When the calcium salt is distilled with lime, a sublimate of large, orange-yellow needles of tribenzoylenebenzene (truxenequinone),



(Michael, A., 1906, i, 518) is formed. On heating the acid for three or four hours with the theoretical amount of potassium permanganate in a large excess of 2% sodium hydroxide, it is oxidised to dicarboxyphenylglyoxylic acid, $C_6H_3(CO_2H)_2 \cdot CO \cdot CO_2H$ (Graebe and Bossel, A., 1896, i, 436), and an acidic by-product, but complete oxidation with an excess of permanganate results in the formation of hemimellitic acid (Graebe and Leonhardt, A., 1896, i, 437). The constitution of decacycene is therefore represented by the annexed formula.

J. C. W.

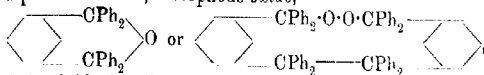
Strain Laws of Ring Systems. OSCAR HINSBERG (*J. pr. Chem.*, 1913, 88, [ii], 58—60).—It has been shown previously (A., 1902, i, 238; 1904, i, 200) from a comparison of the stability of various azines and acridine derivatives, that the strain in tertiary ring systems, composed of 6-membered rings arranged in linear order, increases rapidly with the complexity of the molecule, so that a system containing five conjugated rings is either very unstable or incapable of existence.

The author refers to the unsuccessful attempts of W. A. and M. Mills (T., 1912, 101, 2194) to prepare dinaphanthracene by the oxidation of its di- and tetra-hydro-derivatives in support of this view, and points out that their work renders it probable that the strain laws, developed by him for ring-systems containing carbon and nitrogen, are also applicable to systems composed wholly of carbon rings.

F. B.

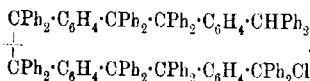
Metaquinonoids. II. OTTO STARK and O. GARBEN (*Ber.*, 1913, 46, 2252—2259).—The possibility that the yellow hydrocarbon, obtained previously (this vol., i, 362) by the removal of halogen from tetraphenyl-*m*-xylylene dichloride, is a triarylmethyl derivative and not a true metaquinonoid compound, is excluded on account of the comparatively great stability of the hydrocarbon towards air and oxygen, and its inability to form additive compounds with ether, ethyl acetate, benzene, alcohol, acetic acid, and acetic anhydride.

A benzene solution of the hydrocarbon, after being exposed to air for eight weeks, and occasionally treated with oxygen during this time, deposited a white, amorphous *oxide*,



which is insoluble in all the usual solvents with the exception of hot nitrobenzene, and when heated becomes discoloured and slowly decomposes at 200°, the decomposition being complete at 250°.

On treatment with hydrogen chloride in benzene, it yields an additive compound formed by the union of four molecules of the hydrocarbon with one of hydrogen chloride. This compound crystallises in white needles, m. p. 286—287° (decomp.), with previous darkening at 275°, and is considered to have the following constitution:



It dissolves in boiling benzene, yielding deep yellow solutions, but the molecular weight in these solutions is only half that corresponding with the above formula. The authors interpret these results as indicating that the substance undergoes dissociation, at the position shown by the dotted line, into two triarylmethyl residues.

During the preparation of the hydrocarbon, an isomeride was obtained (*loc. cit.*) which had a higher m. p., and was supposed to be identical with Thiele's tetraphenyl-*p*-xylylene. The identity of the two compounds has now been fully established. The simultaneous

formation of the para-quinonoid hydrocarbon is due, however, not to a wandering of the groups in the meta-compound as was imagined previously, but to the original methyl isophthalate, from which the hydrocarbon was prepared, being contaminated by considerable quantities of methyl terephthalate.

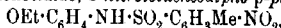
The *diethyl ether* of tetraphenyl-*m*-xylylene glycol, prepared by boiling the corresponding chloride with alcohol, has m. p. 116—117°; the *methyl ether*, m. p. 103—104°. The *diacetyl* derivative, prepared from the glycol and acetic anhydride, has m. p. 90—91.5°.

Tetraphenyl-*p*-xylylene glycol crystallises from glacial acetic acid in well developed prisms, m. p. 168—169°, containing the solvent (1 mol.), which is removed by heating the crystals under diminished pressure at 130—140°; the glycol then has m. p. 171—171.5°. The *diacetyl* derivative sinters at 198°, m. p. 203—204°.

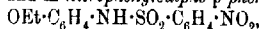
Tetraphenyl-p-xylylene dichloride, prepared by passing hydrogen chloride into an acetic acid solution of the glycol, crystallises in slender, flat prisms, m. p. 239—240°, with previous sintering and darkening.

F. B.

Nitro-derivatives of *p*-Phenetidine. FRÉDÉRIC REVERDIN and LUDWIG FÜRSTENBERG (*Arch. Sci. phys. nat.*, 1913, **35**, 594—605; *Bull. Soc. chim.*, 1913, [iv], **13**, 671—681).—The present work has been undertaken in continuation of the experiments of Reverdin and de Luc (*A.*, 1909, i, 377, 913) on the nitration of *p*-anisidine. The initial materials in the various experiments are aceto-*p*-phenetidine, toluenesulpho-*p*-phenetidine, *o*-nitrotoluenesulpho-*p*-phenetidine,



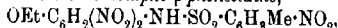
needles, m. p. 128°, and *m*-nitrophenylsulpho-*p*-phenetidine,



prismatic needles, m. p. 129—130°, the two latter substances being obtained by the action of the corresponding chlorides on an alcoholic solution of *p*-phenetidine in the presence of sodium acetate.

2 : 3-Dinitro-*p*-phenetidine (compare Wender, *A.*, 1890, 751) is formed by the action of concentrated sulphuric acid on 2 : 3-dinitro-*p*-toluenesulphophenetidine, white needles, m. p. 163°, obtained by the addition of nitric acid (D 1.52) to a solution of toluenesulpho-*p*-phenetidine in glacial acetic acid.

3 : 5-Dinitro-*o*-nitrotoluenesulpho-*p*-phenetidine,



slender needles, m. p. 163°, is prepared by the action of nitric acid (D 1.4) on a solution of *o*-nitrotoluenesulpho-*p*-phenetidine in glacial acetic acid. Energetic treatment with concentrated sulphuric acid converts it into 3 : 5-dinitro-*p*-aminophenol, m. p. 230°, from which the position of the nitro-groups is ascertained, whilst a milder treatment leads to the formation of 3 : 5-dinitro-*p*-phenetidine, red leaflets, m. p. 138—139°. The same base can be obtained by the saponification of the product formed when 3-nitrotoluenesulpho-*p*-phenetidine is nitrated in acetic acid solution.

When phenacetine is nitrated in sulphuric acid solution under definite conditions, 2 : 6-dinitro-*p*-phenacetine, $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{NHAc}$, white needles, m. p. 148°, is formed, which, when hydrolysed by dilute

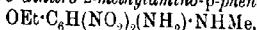
sulphuric acid, is converted into 2:6-dinitro-*p*-phenetidine, yellow leaflets, m. p. 172°. The constitution of the base follows from the identity with the product obtained by the ethylation of isopicramic acid.

Unsuccessful attempts have been made to prepare 2:5-dinitro-*p*-phenetidine by the nitration of phenacetine or of *m*-nitrobenzenesulpho-*p*-phenetidine. In the latter case, the main product of the change was a 2:3-dinitro-derivative, m. p. 178°, which, on hydrolysis, yielded 2:3-dinitro-*p*-phenetidine, smaller quantities of a 3:5-dinitro-derivative being also formed.

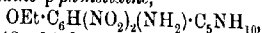
2:3:5-Trinitrotoluenesulpho-*p*-phenetidine, white needles, m. p. 217°, is prepared by nitrating 2:3-dinitrotoluenesulpho-*p*-phenetidine, and, when acted on by sulphuric acid, yields 2:3:5-trinitro-*p*-phenetidine, fine red needles with green reflex, m. p. 126—127°. The constitution of this substance is deduced from its analogy with the trinitro-*p*-anisidine obtained by Reverdin (A., 1910, i, 470) in which the nitro-groups are in the 2:3:5-positions, that in position 2 being mobile (compare Meldola and Kuntzen, T., 1910, 97, 444). This is established by converting it into dinitroguaiacol, dinitrocatechol, and dinitroveratrole of known constitution.

2:3:5-Trinitroaceto-*p*-phenetidine, $\text{OEt}\cdot\text{C}_6\text{H}(\text{NO}_2)_3\cdot\text{NHAc}$, white needles, m. p. about 245°, is obtained by the action of acetic anhydride and a trace of concentrated sulphuric acid on the free amine.

The following derivatives have been prepared by the replacement of the mobile nitro-group of 2:3:5-trinitro-*p*-phenetidine; 3:5-dinitro-2-anilino-*p*-phenetidine, $\text{OEt}\cdot\text{C}_6\text{H}(\text{NO}_2)_2(\text{NH}_2)\cdot\text{NHPh}$, brown leaflets, m. p. 151—152°; 3:5-dinitro-2-methylamino-*p*-phenetidine,



red needles, m. p. 166—167°; 3:5-dinitro-2-dimethylamino-*p*-phenetidine, $\text{OEt}\cdot\text{C}_6\text{H}(\text{NO}_2)_2(\text{NH}_2)\cdot\text{NMe}_2$, m. p. 119—120°; 3:5-dinitro-2-phenoxy-*p*-phenetidine, $\text{OEt}\cdot\text{C}_6\text{H}(\text{OPh})(\text{NO}_2)_2\cdot\text{NH}_2$, red needles, m. p. 185—186°; 3:5-dinitro-2-amino-*p*-phenetidine, $\text{OEt}\cdot\text{C}_6\text{H}(\text{NO}_2)_2(\text{NH}_2)_2$, m. p. 250°; 3:5-dinitro-2-piperidino-*p*-phenetidine,



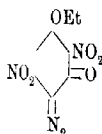
red leaflets, m. p. 143—144°.

2:5-Dinitro-1-ethoxy-3:4-quinonediazide (annexed formula: compare

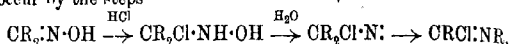
Meldola and Reverdin, T., 1910, 97, 1204) is formed by the addition of sodium nitrite to a solution of 2:3:5-dinitro-*p*-phenetidine in sulphuric acid. It separates from acetic acid in orange prisms, m. p. 186°.

3:5-Dinitro-2-hydroxy-*p*-phenetidine, brown needles or blackish crystals with green metallic reflex, m. p. 166—167°, is prepared by boiling a solution of 2:3:5-trinitro-*p*-phenetidine in acetone with an alcoholic solution of sodium acetate. When the amino-group is removed in the usual manner, 3:5-dinitro-2-hydroxyphenetole, yellow leaflets, m. p. 155°, is obtained, the *barium* and *silver* salts of which were also examined. The latter, when treated with an alcoholic solution of ethyl iodide, yields slightly impure 3:5-dinitro-1:2-diethoxybenzene, m. p. 90—91°, probably identical with the product described by Blanksma (A., 1905, i, 431) to which the m. p. 94—95° is now assigned.

H. W.



The Molecular Rearrangement of Triphenylmethylhydroxylamine. JULIUS STIEGLITZ and PAUL N. LEECH (*Ber.*, 1913, 46, 2147—2151).—In accordance with Stieglitz's views as to the molecular rearrangement of bromoamides, hydroxamic acids, etc. (*A.*, 1897, i, 43), which regard the Beckmann rearrangement with an oxime to occur by the steps



it is found that triphenylmethylhydroxylamine, $\text{CPh}_3\text{:NH}\cdot\text{OH}$, which in constitution closely resembles the first class of product in the above series of changes, when treated in ethereal solution with phosphorus pentachloride is converted into benzophenoneanil, $\text{CPh}_2\text{:NPh}$, m. p. 111—112°. The above course of the rearrangement is thus confirmed.

D. F. T.

The Molecular Rearrangement of Triphenylmethylbromoamine. JULIUS STIEGLITZ and ISABELLE VOSBURGH (*Ber.*, 1913, 46, 2151—2156).—In an endeavour to decide which of the tautomeric forms $\text{R}\cdot\text{CO}\cdot\text{NMX}$ and $\text{R}\cdot\text{C}(\text{OM})\cdot\text{NX}$ (M =metal, X =halogen) of the metallic salts of the halogenamides is to be regarded as the intermediate stage in the production of amines from halogen-amides by Hofmann's rearrangement, the authors have prepared and examined triphenylmethylbromoamine, $\text{CPh}_3\text{:NHBr}$, with which the possibility of tautomerism is excluded. By the action of alkali, the elements of hydrogen bromide are eliminated from this substance with formation of benzophenoneanil. The series of changes must therefore be $\text{CPh}_3\text{:NHBr} \rightarrow \text{CPh}_3\text{:NMBr} \rightarrow \text{CPh}_2\text{:N:} \rightarrow \text{CPh}_2\text{:NPh}$. The former of the alternative structures thus receives support without excluding the possibility of the second formula being the correct one for the structure involved.

Triphenylmethylbromoamine, colourless crystals, m. p. 63°, was obtained by the action of bromine on triphenylmethylamine in chloroform solution in the presence of sodium hydroxide solution. By heating with soda-lime at 100—120°, or with a hot methyl alcoholic solution of sodium methoxide, it is converted into benzophenoneanil, m. p. 111—112°.

When heated to its m. p., triphenylmethyldichloroamine rapidly loses chlorine with the formation of benzophenoneanil with a little chlorobenzophenoneanil.

D. F. T.

Oxidation of Organic Developers with Silver Salts. *p*-Aminophenol and Metol. FRITZ KROPP (*J. pr. Chem.*, 1913, [ii], 88, 73—77).—On the addition of silver nitrate to an aqueous solution of *p*-aminophenol or *p*-methylaminophenol, the liquid acquires a bluish-violet colour and benzoquinone is produced.

In ammoniacal solution a blue coloration is produced, but no definite compound could be isolated from the reaction product.

When dissolved in aqueous sodium hydroxide and treated with silver bromide, *p*-aminophenol yields a substance which crystallises in brown leaflets having a metallic glaucous, m. p. 194° (not sharp), and gives a dark blue coloration on treatment with phenol and ammonia.

The addition of silver bromide to a solution of *p*-aminophenol in aqueous sodium hydroxide and in the presence of potassium metadisulphite results in the formation of a small amount of a white substance, which is probably a sulphonic acid; under similar conditions netol yields a strongly green fluorescent solution, but no definite compound could be isolated.

The amount of silver reduced in the above reactions, and also the amount of sulphite which disappears, depends on the conditions under which the reduction is carried out. F. B.

Nitration of Anisole to Trinitroanisole. ALFRED L. BROADBENT and FIN SPARRE (*Eighth Inter. Cong. App. Chem.*, 1912, 4, 15—17).—No experimental details of the preparation of 2:4:6-trinitroanisole from anisole appear to have been published; the literature contains merely statements that the nitration is possible.

After considerable difficulties, the authors have evolved the following details which permit a yield of 85% of that theoretically expected from the anisole taken.

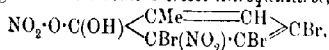
A mixture of 130 grams of nitric acid (D 1.52) with 220 grams of sulphuric acid (D 1.84), which is mechanically agitated by a stirrer, is cooled to -5° by immersion in a freezing mixture of ice and salt whilst 30 grams of anisole are added in small drops. The addition should occupy two to three hours, and the temperature of the mixture should never reach 0° . After all the anisole has been introduced, the temperature is raised to $65-70^{\circ}$ for twenty minutes with continued stirring, and the mixture is then poured into water. After washing with warm water and dilute sodium carbonate solution successively, with subsequent drying, the product has m. p. $64-65^{\circ}$, D²⁰ 1.408, and is slowly hydrolysed by water to methyl alcohol and picric acid.

D. F. T.

Hydrolysis of Trinitroanisole by Alkalis and Water. WALTER E. MASLAND and FIN SPARRE (*Eighth Inter. Cong. App. Chem.*, 1912, 4, 77).—Pure trinitroanisole is hydrolysed fairly rapidly by hot solutions of the alkali carbonates and slowly by hot water; the action of each of these in the cold is much more feeble. Picric acid is produced in each case.

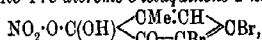
D. F. T.

Action of Nitric Acid on Halogen Derivatives of *o*-Alkylphenols. II. Nitric Acid Derivatives of 3:4:5- and 3:5:6-Tribromo-*o*-cresols. THEODOR ZINCKE and NELSON W. JANNEY (*Annalen*, 1913, 398, 343—353).—3:4:5- and 3:5:6-Tribromo-*o*-cresols react with nitric acid in the sense of the equation: $C_6H_2Br_3 + 2HNO_3 = C_6H_2O_2N_2Br_3 + H_2O$, but the two products exhibit quite different behaviour. 3:4:5-Tribromo-*o*-cresol and nitric acid, D 1.48, yield by keeping 3:4:5-tribromo-*o*-cresol nitroquininol,



m. p. 126° (decomp.), colourless needles, which is not reconverted into the tribromo-*o*-cresol by reduction, yields tribromo-*p*-toluquinone by warming with concentrated sulphuric acid, and by boiling with

toluene, glacial acetic acid, or tetrachloroethane is converted by loss of nitrosyl bromide into 4:5-dibromo-*o*-toluquinone 2-nitrate,



m. p. 173° (decomp.), pale yellow prisms. The latter is stable, dissolves in alkalis, and is reduced by stannous chloride, hydrochloric acid, and a little alcohol, to 4:5-dibromo-2:3-dihydroxytoluene, m. p. 104°, colourless needles, which forms a *diacetyl* derivative, m. p. 137—138°, and is oxidised by nitric acid, D 1.15, to 4:5-dibromo-*o*-toluquinone, $\text{C}_7\text{H}_4\text{O}_2\text{Br}_2$, m. p. 96—98°, dark red, crystalline powder.

3:5:6-Tribromo-*o*-cresol and nitric acid, D 1.48, at 0° yield 3:5:6-tribromo-*o*-cresolnitroquinol, $\text{NO}_2 \cdot \text{O} \cdot \text{C}(\text{OH}) \begin{array}{c} \text{CBr} = \text{CH} \\ \diagup \quad \diagdown \\ \text{CMe}(\text{NO}_2) - \text{CBr} \end{array} \text{CBr}$, m. p. 96° (decomp.), faintly yellow leaflets or needles, which regenerates the tribromo-*o*-cresol by reduction with stannous chloride solution after being initially heated with glacial acetic acid for a short time. C. S.

Bromo-derivatives of *o*-Cresol. NELSON W. JANNEY (*Annalen*, 1913, 398, 354—372).—The author describes the preparation of some of the unknown brominated *o*-cresols; usually the constitutions are determined by converting the substance ultimately into a quinone of the ortho- or of the para series.

4-Bromo-*o*-cresol, m. p. 80°, broad needles, prepared from diazotised 4-bromo-*o*-toluidine in the usual manner, forms a *benzoate*, m. p. 41°, and is converted by nitric acid, D 1.4, in glacial acetic acid into a *nitro*- and a *dinitro*-derivative, the latter, m. p. 169°, crystallising in yellow prisms.

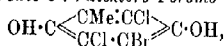
3:4-Dibromo-*o*-cresol, m. p. 94—95°, colourless needles, is obtained by brominating 4-bromo-*o*-cresol in chloroform in the presence of a little iron. It forms an *acetate*, m. p. 49°, is converted by nitric acid, D 1.52, in glacial acetic acid into the preceding bromo-dinitro-*o*-cresol, and yields 3:4-dibromo-5-nitro-*o*-cresol (see below) by treating its solution in glacial acetic acid with powdered sodium nitrite. 3:6-Dibromo-*o*-cresol, m. p. 38° (*benzoate*, m. p. 104°, white needles), is prepared in a similar manner from 6-bromo-*o*-cresol. Its constitution follows from the fact that it yields only oily products by treatment with sodium nitrite and acetic acid; were it 5:6-dibromo-*o*-cresol, it must have yielded 5:6-dibromo-3-nitro-*o*-cresol identical with that obtained from 3:5:6-tribromo-*o*-cresol (see below).

3:5-Dibromo-*o*-cresol is already known. By treatment with sodium nitrite and acetic acid at 12—15°, it is converted into 5-bromo-3-nitro-*o*-cresol, by the reduction of which 5-bromo-3-amino-*o*-cresol (*diacetyl* derivative, m. p. 203°) is obtained. The hydrochloride of the last substance, dissolved in glacial acetic and concentrated hydrochloric acids, is converted by moist chlorine into the *diketo-chloride*, $\text{CClBr} \begin{array}{c} \text{CCl} \cdot \text{CMe} \\ \diagup \quad \diagdown \\ \text{CCl}_2 - \text{CO} \end{array} \text{CO}$, m. p. 80°, stout, yellow prisms, by the reduction of which by stannous chloride 4:6-dichloro-5-bromo-2:3-dihydroxytoluene, m. p. 186°, colourless needles (*diacetate*, m. p. 176—177°), is obtained. By oxidation with nitric acid, D 1.4, the last compound is

converted into 4:6-dichloro-5-bromo-o-toluquinone, m. p. 121—122°, red, crystalline powder.

By treatment with nitric acid, D 1·4, and glacial acetic acid, 3:5-dibromo-o-cresol yields Auwers' 3-bromo-5-nitro-o-cresol, and finally 3:5-dinitro-o-cresol. By reduction with alcohol and stannous chloride, the former is converted into 3-bromo-5-amino-o-cresol, m. p. 146°, stout prisms (acetyl derivative, m. p. 152°; diacetyl derivative, m. p. 167°), from the hydrochloride of which 3-bromo-p-toluquinone is obtained by oxidation with potassium dichromate and dilute sulphuric acid.

3:4:5-Tribromo-o-cresol, m. p. 89° (not 79°, as stated in the literature), which is only occasionally obtained pure by the bromination of o-cresol, is prepared in 90—95% yield by the action of bromine and iron on 4-bromo-o-cresol in cold chloroform. It is most conveniently obtained by treating a solution of 3:5-dibromo-o-cresol in glacial acetic acid with 10% calcium hypobromite, and warming the resulting keto-bromide, $C_7H_5OBr_2$, m. p. 110° (decomp.), yellow prisms, with concentrated sulphuric acid. The action of sodium nitrite and glacial acetic acid on 3:4:5-tribromo-o-cresol yields Zincke and Hedenström's 3:4-dibromo-5-nitro-o-cresol, which by successive reduction, conversion into the diketo-chloride, and reduction is converted into 3:6-dichloro-4-bromo-p-toluquinol,



m. p. 200—201°, white prisms or needles (diacetate, m. p. 226—227°). By oxidation with nitric acid, the quinol is converted into 3:6-dichloro-4-bromo-p-toluquinone, m. p. 233°, yellow, hexagonal leaflets. The production of a para-quinone proves the constitution of 3:4:5-tribromo-o-cresol and also of 3:4-dibromo-o-cresol.

3:5:6-Tribromo-o-cresol, m. p. 91°, prismatic needles (acetate, m. p. 76—77°), is prepared from 6-bromo-o-cresol in a similar manner as 3:4:5-tribromo-o-cresol from 4-bromo-o-cresol. By treatment with sodium nitrite and glacial acetic acid at 12—15°, it yields 5:6-dibromo-3-nitro-o-cresol, m. p. 100°, pale yellow needles (acetate, m. p. 74°), from which 4:6-dichloro-5-bromo-2:3-dihydroxytoluene and 4:6-dichloro-5-bromo-o-toluquinone, identical with the corresponding substances obtained from 3:5-dibromo-o-cresol, are obtained by reduction and treatment of the keto-chloride in the usual manner.

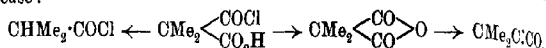
C. S.

[1-Methylcyclopentane-1 carboxylic Acid.] I. PETROV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 644).—For this acid the author finds the constants, b. p. 216—217°, D_4^{20} 1·0386 (compare Tschitschibabin, this vol., i, 467).

T. H. P.

Four Different Anhydrides of Dibenzylacetic Acid. The Catalytic Action of Metaphosphoric Acid on Acid Chlorides. HERMANN LEUCHS, JOHANNES WUTKE, and ERICH GIESELER (*Ber.*, 1913, 46, 2200—2215).—According to Staudinger and Ott (*A.*, 1908, i, 602) the action of thionyl chloride on malonic acids results primarily in the formation of the semi-chlorides which may subsequently part with carbon dioxide to give the acetyl chlorides, or lose hydrogen chloride

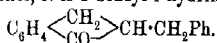
to form malonic anhydrides and finally ketens, as in the following case:



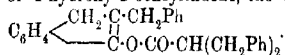
In the case of dibenzylmalonic acid, the chief product is dibenzylacetyl chloride, but a by-product is also formed which is a simple polymeride of dibenzylketen and is shown to be tetrabenzylcyclobutan-1:3-dione, $\text{C}(\text{CH}_2\text{Ph})_2 \begin{array}{c} \text{CO} \\ \text{CO} \end{array} \text{C}(\text{CH}_2\text{Ph})_2$. That its formation is due to the intervention of dibenzylketen is assumed from the fact that the substance could not be obtained from dibenzylacetic acid or dibenzylacetyl chloride.

In order to moderate the action of thionyl chloride, with the hope of obtaining the semi-chloride of dibenzylmalonic acid, the reagent was diluted with ether, but it was found that the action was too moderate, the product being the ordinary anhydride of dibenzylacetic acid, $[\text{CH}(\text{CH}_2\text{Ph})_2\text{CO}]_2\text{O}$.

Attempts were made to prepare the cyclobutane derivative from dibenzylacetyl chloride. When this substance was heated at 250° , it gradually parted with hydrogen chloride, but the product was a third anhydride, m. p. 145° . In some experiments on the preparation of the chloride, it was found that, unless an excess of phosphorus pentachloride was employed, the metaphosphoric acid, or some similar product from the phosphoryl chloride, exerted a catalytic influence on the elimination of hydrogen chloride, so that, on distillation in a vacuum, very little acid chloride was obtained, the chief product being a fourth, oily anhydride. This recalls the formation of bis- α -hydrindone (2:2)-spiran by the action of phosphorus pentachloride on dibenzylmalonic acid (A., 1912, i, 179), in which case it is now found that the yield can be improved by the above process. Since the oil forms a hydrazone and is similar in deportment to methyl-, ethyl- and phenyl- α -hydrindones, it is 2-benzyl-1-hydrindone,



The solid anhydride, m. p. 145° , is bimolecular, does not yield a hydrazone, forms dibenzylacetic acid and 2-benzylhydrindone on hydrolysis with alcoholic potassium hydroxide, and dibenzylacetyl chloride and 2-chloro-2-benzyl-1-hydrindone under the influence of phosphorus pentachloride. It is therefore the *O*-dibenzylacetyl derivative of 1-hydroxy-2-benzylindene, the enolic form of 2-benzylhydrindone,



Dibenzylmalonic acid was boiled with thionyl chloride, and, after distilling off the dibenzylacetyl chloride at 203° – $204^\circ/15$ mm., the residue was extracted with light petroleum, leaving a 10% yield of tetrabenzylcyclobutan-1:3-dione, $\text{C}_{32}\text{H}_{28}\text{O}_2$, which crystallised from benzene in colourless, light needles, m. p. 249° – 251° , and sublimed at 220° – $230^\circ/18$ mm. When hydrolysed by alcoholic sodium hydroxide, it gave *s*-tetrabenzylacetone, $\text{CO}[\text{CH}(\text{CH}_2\text{Ph})_2]_2$, in the form of well-defined prisms, m. p. 124.5° – 125.5° (compare tetraphenylacetone,

ger, A., 1911, i, 306). The ordinary *dibenzylacetic anhydride*, $C_{22}H_{20}O_3$, crystallised from alcohol in prisms, m. p. 75–76°, and formed dibenzylacetamide and ammonium dibenzylacetate when treated with ammonia in ether.

Dibenzylacetyl chloride, $C_{16}H_{15}OCl$, was prepared by the action of thionyl chloride on dibenzylacetic acid. The residue after distillation contained a little of the true anhydride, m. p. 75–76°, but no cyclobutane derivative. The chloride is a viscous, almost colourless oil, b. p. 150°/0.25 mm., and the pale yellow, crystalline mass described by Schneidewind (A., 1888, 704), was probably not dibenzylacetyl chloride. After heating the oil for an hour at 245–255° in a low vacuum, and subsequently distilling off the unchanged chloride in a high vacuum, the residue was extracted with chloroform, precipitated by petroleum, and the 1-*dibenzylacetoxy-2-benzylindene*, $C_{32}H_{28}O_2$, was recrystallised from benzene in the form of shining, four or six-sided leaflets, m. p. 144–145°. On oxidation it yielded benzoic and phthalic acids and benzaldehyde, and on treatment with phosphorus pentachloride in chloroform suspension, it gave dibenzylacetyl chloride and

2-chloro-2-benzylhydrindone, $C_8H_7 \begin{smallmatrix} \text{CH}_2 \cdot \text{CCl} \cdot \text{CH}_2 \cdot \text{Ph} \\ \text{CO} \end{smallmatrix}$. The latter is insoluble in cold petroleum, forms long, colourless, glistening leaflets, m. p. 74–75°, and may be prepared by passing chlorine into a chloroform solution of 2-benzylhydrindone.

When dibenzylacetic acid is treated with a slight excess of phosphorus pentachloride, the chief product is the acid chloride, but when an insufficient amount of the reagent is employed and the product is evacuated at 200–250°, hydrogen chloride is eliminated and 2-benzylhydrindone distils over, mixed with a little unchanged acid. The distillate is added to an ethereal solution of ammonia, filtered, and re-distilled, giving a yellow, viscous, almost odourless oil, b. p. 223.5–224.5° (corr.)/20 mm. Phosphorus pentachloride converts it into 1-chloro-2-benzylindene, $C_8H_7 \begin{smallmatrix} \text{CH}_2 \\ \text{CCl} \end{smallmatrix} \gg \text{C} \cdot \text{CH}_2 \cdot \text{Ph}$, which crystallises

in massive prisms, m. p. 64–65°, b. p. 206°(corr.)/13 mm., and yields benzaldehyde and benzoic and phthalic acids on oxidation. Its dibromide, $C_{16}H_{13}ClBr_2$, forms massive, sparkling, six-sided plates, m. p. 97–98°, which are hydrolysed in aqueous alcohol to 2-bromo-2-benzylhydrindone, $C_{16}H_{13}OBr$. The latter is best obtained by the action of bromine on β -benzylhydrindone, and forms colourless, sparkling, six-sided leaflets or prisms, m. p. 80–81°.

The phenylhydrazone of 2-benzylhydrindone, $C_{22}H_{20}N_2$, crystallises in light yellow, four-sided tablets, and, like the hydrazone of hydrindone itself (Kipping, T., 1894, 65, 493), it has not a constant m. p. When the ketone is heated to 130° with an excess of phenylhydrazine, however, a product, $C_{28}H_{26}N_2$, is obtained in short, colourless prisms or tablets, m. p. 190–192°.

J. C. W.

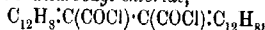
[Polymerisation.] CARL LIEBERMANN (*Ber.*, 1913, 46, 2084–2086).—Polemical. A reply to Kronstein (this vol., i, 725).

D. F. F.

Some Derivatives of Diphenyleneacetic [Fluorene-9-carboxylic] Acid and Bisdiphenylenesuccinic [9:9'-difluoryl-9:9'-dicarboxylic] Acid. ROBERT STOLLÉ and F. WOLF (*Ber.*, 1913, 46, 2248—2252).—The action of thionyl chloride on fluorene-9-carboxylic acid leads to the formation of fluorene-9-carboxyl chloride, 9-chlorofluorene-9-carboxyl chloride, and 9:9'-difluoryl-9:9'-dicarboxyl chloride, according to the condition under which the action is carried out.

When heated for one to two hours with thionyl chloride in carbon tetrachloride solution, fluorene-9-carboxylic acid yields the corresponding chloride, which has m. p. 77° and reacts with ammonia and aniline yielding the amide, m. p. 251°, and anilide (compare Vorländer and Fritzche, this vol., i, 724, and Staudinger, A., 1906, i, 861).

9:9'-Difluoryl-9:9'-dicarboxyl chloride,



obtained together with fluorene-9-carboxyl chloride by heating fluorene-9-carboxylic acid for several hours with thionyl chloride, forms colourless crystals, m. p. 213° (decomp.), and decomposes into bisdiphenylene-ethane (9:9'-difluoryl; Graebe and Mantz, A., 1896, i, 442) when heated with concentrated hydrochloric acid. It is also produced by passing chlorine into a boiling solution of fluorene-9-carboxyl chloride in carbon tetrachloride. It reacts with sodium methoxide and sodium ethoxide, yielding the methyl ester, m. p. 237° (Kolvenbach, *Diss.*, Königsberg, 1897), and ethyl ester respectively (compare Staudinger, A., 1906, i, 825); the anilide forms a colourless powder, m. p. 250°.

If the action of thionyl chloride on fluorene-9-carboxylic acid or its chloride is continued for 200 hours, 9-chlorofluorene-9-carboxyl chloride (Klinger, A., 1912, i, 558) is produced.

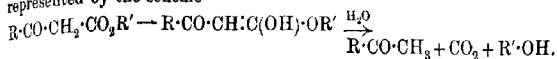
Prolonged heating leads to the decomposition of thionyl chloride into chlorine and sulphur monochloride: $4\text{SOCl}_2 = 2\text{SO}_2 + 3\text{Cl}_2 + \text{S}_2\text{Cl}_2$. It is possible that the chlorinating action of thionyl chloride mentioned above is to be referred to this decomposition, but whether the formation of 9:9'-difluoryl-9:9'-dicarboxyl chloride is due to the direct oxidation of fluorene-9-carboxyl chloride, or to the interaction of the latter compound with 9-chlorofluorene-9-carboxyl chloride, has not yet been determined.

F. B.

New Method for the Ketonic Decomposition of β -Ketonic Esters. HANS MEERWEIN (*Annalen*, 1913, 398, 242—250).—When heated at 200° with 0.5—1 volume of water, esters of β -ketonic acids undergo the ketonic decomposition quantitatively or nearly so. That the change is not due to an ordinary hydrolysis of the ester and subsequent elimination of carbon dioxide is proved by the fact that only those β -ketonic esters which are capable of enolising undergo the change. It is very probable that the enolic modification is the form which is concerned in the decomposition, since the facility with which the ketone is produced runs *pari passu* with the tendency of the β -ketonic ester to enolise; thus, strongly acidic, cyclic β -ketonic esters such as ethyl succinosuccinate are decomposed most readily, then follow acyclic, non-alkylated esters such as ethyl acetoacetate and benzoyl-

acetate, and finally alkylated esters such as ethyl benzyl-, methyl-, or ethyl-acetoacetate, in the last case a temperature of 250° being requisite.

The author is of opinion that the course of the decomposition is represented by the scheme



In support of this opinion are the facts that ethyl benzylmalonate is converted into ethyl β -phenylpropionate, and ethyl α -gamma-ethoxyglutaconate into ethyl glutaconate, by water at 250° and 200° respectively.

The following changes are described: methyl 1-phenylcyclohexan-3-one-4-carboxylateacetate into methyl 1-phenylcyclohexan-3-one-5-acetate (A., 1908, i, 545), methyl cyclopentanone-2-carboxylate into cyclopentanone, ethyl succinosuccinate into cyclohexan-1:4-dione, methyl benzoylacetate into acetophenone, ethyl acetoacetate into acetone, ethyl benzylacetoacetate into methyl β -phenylethyl ketone, ethyl methylacetoacetate into methyl ethyl ketone, and ethyl ethyl-acetoacetate into methyl propyl ketone. C. S.

Action of Hydroxylamine on Ketones of the Type
 $R\cdot CH\cdot CH\cdot CH\cdot CH\cdot CO\cdot R$. V. RICCARDO CUSCA and G. B. BERNARDIS
 (Atti R. Accad. Lincei, 1913, [v], 22, i, 708—711. Compare A., 1910, i, 684).—The substance $C_{26}H_{24}O_8N_4$, m. p. 213° , mentioned in the paper cited, contains one molecule of alcohol of crystallisation; it does not react with bromine or with benzaldehyde, and it dissolves in alkalis. It is therefore composed of two molecules of the hydroxylamineoxime of cinnamylidenepyruvic acid united so as to saturate reciprocally their double linkings. The substance gives an insoluble, green copper salt, and a cherry-red coloration with iron salts; in other respects it does not behave like an hydroxamic acid, and is to be regarded as an α -oximino-acid. The compound immediately yields a sodium salt, $C_{24}H_{20}O_8N_4Na_2$, when treated with sodium carbonate, and this salt yields with acids a substance, $C_{24}H_{23}O_8N_4$, m. p. 205° ; this compound has similar properties to the original one, but does not unite with alcohol. When the substance $C_{24}H_{23}O_8N_4$, EtOH, is boiled with dilute sulphuric acid, the ethyl ester, m. p. 207° , is obtained in small quantity.

When the action between hydroxylamine hydrochloride and ethyl cinnamylidenepyruvate is effected in the presence of sodium acetate, there is produced, in addition to the substance $C_{24}H_{23}O_8N_4$, EtOH, a sparingly soluble sodium salt, $C_{26}H_{24}O_8N_4Na$, which, on treatment with dilute sulphuric acid, furnishes an isomeride of the above-mentioned ethyl ester, m. p. 207° . This isomeride has m. p. 198° , and its properties resemble those of the compound of m. p. 207° .

From the mother liquors of the above reaction, the oxime of ethyl cinnamylidenepyruvate, $C_{14}H_{16}O_3N$, m. p. 181° , can be obtained. This substance is the sole product of the reaction when no sodium acetate is added.

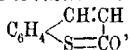
When the sodium salt of the oxime of cinnamylidenepyruvic acid

(*loc. cit.*) is treated with dilute sulphuric acid, the corresponding *cinnamylidene- α -oximinopropionic acid* is produced; it crystallises with $\frac{1}{2}$ H₂O, gives a green copper salt, and a cherry-red coloration with ferric salts. The above-mentioned sodium salt also yields the ethyl ester, m. p. 181°, already described.

R. V. S.

o-Thiolcinnamic Acid. CH. CHMELEWSKI and PAUL FRIEDLÄNDER (*Ber.*, 1913, 46, 1903—1908).—The above substance was prepared in order to examine its tendency to the formation of an anhydride analogous to coumarin; earlier experimental results appear to indicate that unsaturated ring systems of five carbon atoms and one sulphur atom are less easily produced, and are less stable than those corresponding with thiophen, but thiolcinnamic acid closely resembles coumaric acid in its behaviour towards dehydration.

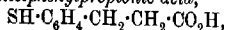
o-Thiolcinnamic acid, SH·C₆H₄·CH:CH·CO₂H, was obtained from *o*-aminocinnamic acid by converting it into the corresponding *thiocyanocompound*, CNS·C₆H₄·CH:CH·CO₂H, needles, m. p. 175°, and then evaporating to dryness its solution in sodium hydroxide, together with sodium sulphide solution. The substance can be obtained more conveniently by introducing the solution of the diazocinnamic acid into a warm concentrated solution of sodium disulphide, and reducing the resultant *dithiocinnamic acid*, (CO₂H·CH:CH·C₆H₄)₂S₂, yellow needles, m. p. 221°, to the thiol acid by the action of zinc dust and sodium hydroxide solution. It was also prepared, through the diazocompound, from the *xanthate*, CO₂H·CH:CH·C₆H₄·S·CS·OEt. *o*-Thiolcinnamic acid, colourless needles, undergoes partial dehydration and oxidation on heating, consequently its m. p., 165°, is not sharp; its *methyl ester* forms tablets, m. p. 114°. *o*-Methylthiolcinnamic acid, SMc·C₆H₄·CH:CH·CO₂H, leaflets, m. p. 176°, obtained by the action of methyl sulphate on an alkaline solution, is more stable than the thiol acid. When heated above its m. p., or, much better, by boiling with acetic anhydride and subsequently distilling in a vacuum, *o*-thiolcinnamic acid is dehydrated to *thiocoumarin* [1:2-benzothiopyrone],



colourless needles, m. p. 80—80.5°, which is volatile with steam, and has an odour surprisingly like that of coumarin itself. It is insoluble in cold solutions of alkali, but dissolves in warm sodium hydroxide, and can be precipitated unaltered by mineral acids. As the acid undergoes isomeric change more readily than the corresponding coumaric acid, the warming with alkali must not be prolonged, otherwise *thiocoumarinic acid* is produced, of which the derived *methylthiolcoumarinic acid* has m. p. about 136°.

In behaviour towards oxidation, *o*-thiolcinnamic acid differs markedly from *o*-coumaric acid. Although frequently oxidation yields the corresponding dithio-acid, oxidation by ferric salts in neutral solution or, better, by potassium ferricyanide in alkaline solution causes elimination of hydrogen and of carbon dioxide with separation of thionaphthen, C₆H₄ < $\begin{array}{c} \text{CH} \\ \diagdown \quad \diagup \\ \text{S} \end{array}$ > CH.

Reduction of *o*-thioleinnamic acid in alkaline solution by sodium amalgam produces *o*-thiolphenylpropionic acid,



colourless needles, m. p. 118° , which above their m. p., or when heated with diluted sulphuric acid, undergo dehydration to *thiohydro-coumarin* [*dihydro-1:2-benzthiopyrone*], $\text{C}_6\text{H}_4 \cdot \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{S} \quad \text{CO} \end{array}$, an oil of pleasant odour.

D. F. T.

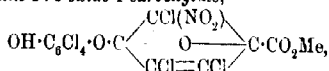
Preparation of Tyrosine. ELI K. MARSHALL, jun. (*J. Biol. Chem.*, 1913, 15, 85—86).—The usual method of preparing tyrosine from silk is laborious and expensive. The method recommended is to obtain it from a pancreatic digest of caseinogen. The fluid on cooling deposits an abundant crystalline yield of tyrosine.

W. D. H.

Action of Nitric Acid on Heptachloro-*o*-quinocatechol Hemiother. C. LORING JACKSON and GEORGE L. KELLEY (*Amer. Chem. J.*, 1913, 49, 435—473).—When heptachloro-*o*-quinocatechol hemiother, $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{O} \cdot \text{C}_6\text{Cl}_4 \cdot \text{O}_2$ (Jackson and Carleton, A., 1908, i, 428), is warmed with glacial acetic acid and a little fuming nitric acid, the product sometimes yields a compound, m. p. 159 — 165° (decomp.), and sometimes a compound, m. p. 176 — 198° (decomp.); in each case the m. p. depends on the rate of heating.

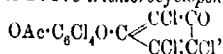
The former compound, m. p. 159 — 165° , is probably the *tetrachlorocatechol hemiother of dichloronitrohydroxycyclopentadienecarboxylic acid*, $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{O} \cdot \text{C}_6\text{Cl}_4(\text{OH})(\text{NO}_2) \cdot \text{CO}_2\text{H}$; it forms white or cream-coloured crystals.

The compound, m. p. 176 — 198° , is regarded as the *tetrachlorocatechol hemiother of 2:4:5-trichloro-2-nitro-1:3-dihydroxycyclopentadiene-1-carboxylic acid*, $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{O} \cdot \text{C}(\text{OH}) \begin{array}{c} \text{CCl}(\text{NO}_2) \cdot \text{C}(\text{OH}) \cdot \text{CO}_2\text{H} \\ \diagup \quad \diagdown \\ \text{CCl} = \text{CCl} \end{array}$; it crystallises in nearly white needles, and is decomposed by boiling water with formation of tetrachlorocatechol, carbon dioxide, an oxide of nitrogen, and a tarry residue. The *methyl ester*, m. p. 221° (decomp.), forms clusters of creamy-white needles. On treating the compound (m. p. 176 — 198°) with methyl alcohol and sulphuric acid, it is converted into the *tetrachlorocatechol hemiother of methyl 2:4:5-trichloro-2-nitrocyclopentene-1:3-oxide-1-carboxylate*,



m. p. 221 — 228° (decomp.), which crystallises in rhombic plates or needles; its *acetyl derivative*, m. p. 189° (decomp.), forms white, rhombic prisms.

When the compound (m. p. 176 — 198°) is heated with acetic anhydride or acetyl chloride, it yields the *acetyl derivative of the tetrachlorocatechol hemiother of 2:4:5-trichlorocyclopentadiene-1-one*,

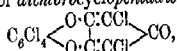


m. p. 165 — 168° , which crystallises in white, lustrous, rhombic plates;

on evaporating the mother liquor from this reaction, a viscous residue is obtained which when dissolved in benzene and treated with pyridine furnishes the *tetrachlorocatechol ether* of 2:5-dichloro-1:1-diacetoxy-cyclopentadiene, $C_6Cl_4O_2 \cdot C_5Cl_2(OAc)_2$, m. p. 188°, which forms white prisms or needles. The *tetrachlorocatechol hemiether* of 2:4:5-tri-

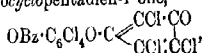
chlorocyclopentadien-1-one, $OH \cdot C_6Cl_4O \cdot C \begin{smallmatrix} \diagup CCl \cdot CO \\ \diagdown CCl \cdot CCl \end{smallmatrix}$, m. p. 182—188°

(decomp.), obtained by hydrolysing the acetyl derivative, crystallises in clusters of white needles. When a benzene solution of this compound or its acetyl derivative is treated with pyridine, the *tetrachlorocatechol ether* of *dichlorocyclopentadienone*,



m. p. 264—272° (decomp.), is obtained, which forms thin, bright red, hexagonal plates and is converted by sodium methoxide into the *tetrachlorocatechol hemiether* of *dichloro-1-hydroxy-1:4-dimethoxycyclopentadiene*, $OH \cdot C_6Cl_4O \cdot C_5Cl_2(OMe)_2 \cdot OH$, m. p. 175—180° (decomp.), which crystallises in white cubes; the corresponding *diethoxy*-compound has m. p. 93°.

By the action of benzoyl chloride on the compound, melting at 176—198°, the *benzoyl* derivative of the *tetrachlorocatechol hemiether* of 2:4:5-trichlorocyclopentadien-1-one,



m. p. 172°, is obtained, which forms white, lustrous scales.

When a solution of hexachloromethoxy-*o*-quinocatechol hemiether, $OH \cdot C_6Cl_4O \cdot C_6Cl_2O_2 \cdot OMe$ (Jackson and Kelley, A., 1912, i, 275), in glacial acetic acid is warmed with fuming nitric acid, it is converted into a substance, m. p. 202—208° (decomp.), which is probably the *tetrachlorocatechol hemiether* of *dichloronitrodihydroxymethoxycyclopentene-carboxylic acid*, $OH \cdot C_6Cl_4O \cdot C_6Cl_2(NO_2)(OH)_2(OMe) \cdot CO_2H$; it forms white crystals, and yields an *acetyl* derivative, m. p. 146° (decomp.).

By the action of glacial acetic acid and fuming nitric acid on hexachloroethoxy-*o*-quinocatechol hemiether (Jackson and Kelley, loc. cit.), a compound, m. p. 210—215° (decomp.), is produced, which crystallises in rhombic plates or prisms, and is provisionally regarded as the *nitric acid* compound of the *tetrachlorocatechol hemiether* of *dichloroethoxy-*o*-quinone*, $OH \cdot C_6Cl_4O \cdot C_6Cl_2O_2 \cdot OEt, HNO_3$. Another substance, m. p. 130—158° (decomp.), was also obtained in this reaction, which seems to be the corresponding compound containing 2HNO₃.

E. G.

Quinonecarboxylic Esters. KARL BRUNNER (*Monatsh.*, 1913, 34, 913—930).—Although esters of substituted *p*-benzoquinone-carboxylic acids are known, previous attempts (von Rakowski and Leppert, A., 1875, 1197; Brunner, *Monatsh.*, 1881, 2, 464; Nef, A., 1887, 255; Juch, A., 1905, i, 701) to prepare *p*-benzoquinone-carboxylic acid have been unsuccessful. Since this failure was possibly attributable to the employment of aqueous solutions, the

author has been led to study the oxidation of methyl gentisate in the absence of water and has thus prepared methyl *p*-benzoquinone-carboxylate and a number of its derivatives.

When a solution of methyl gentisate in benzene is shaken with a mixture of silver oxide and potassium carbonate for five minutes at 40–50°, methyl *p*-benzoquinonecarboxylate, yellowish-red crystals, m. p. 53.5–54°, is obtained. The dry substance may be preserved unchanged for months in the dark. It is rapidly decomposed when warmed with water. When mixed in warm ethereal solution with an equimolecular quantity of methyl gentisate, it is converted into methyl quinhydronecarboxylate, dark red crystals with metallic glance, m. p. 85–86° which, when warmed with sulphurous acid and water, is transformed into methyl gentisate, m. p. 87°. When mixed with aniline in ethereal solution, methyl *p*-benzoquinonecarboxylate, yields methyl dianilino-*p*-benzoquinonecarboxylate, $C_8H_4O_4(NHPh)_2$, deep red, silky needles, m. p. 202–203°.

Methyl cyanoquinolcarboxylate, $C_9H_7O_4N$, is formed when an aqueous solution of sodium cyanide is added to a cold acidified alcoholic solution of methyl *p*-benzoquinonecarboxylate. It has m. p. 225–226°, and dissolves sparingly in ether and benzene to yield solutions which have an intense blue fluorescence. Small quantities of a substance, m. p. above 220°, are obtained as a by-product. When treated with potassium hydroxide and acetic anhydride, methyl cyanoquinolcarboxylate yields a diacetyl derivative, colourless crystals, m. p. 107.5–108°.

Methyl cyanoquinolcarboxylate is converted by concentrated sulphuric acid at 100° into *p*-dihydroxyphthalimide, sulphur-yellow needles, m. p. 273–274°. This substance appears to be in all respects identical with that prepared by Thiele and Meisenheimer (A., 1900, i, 299), from dicyanoquinol, except that it gives up its water of crystallisation with greater readiness. This phenomenon apparently depends to some extent, however, on the size of the crystals. The lead salt, $C_8H_5O_4NPb.H_2O$, carmine needles, is also described.

When methyl cyanoquinolcarboxylate is successively treated with concentrated aqueous potassium hydroxide and sulphuric acid, *p*-dihydroxyphthalic acid is obtained in practically white crystals, m. p. 219–220° (decomp.). The air-dried acid appears to be anhydrous. According to Thiele and Günther (A., 1906, i, 744) it has m. p. 213° and contains $\frac{1}{2}H_2O$. The lead salt, $C_8H_4O_4Pb.\frac{1}{2}H_2O$, crystallises in leaflets. When sublimed in a vacuum at 230–240°, the acid is converted into *p*-dihydroxyphthalic anhydride, yellow, hygroscopic needles, m. p. 232–233° (compare Thiele and Günther, loc. cit.), which yields the corresponding diacetyl derivative, m. p. 156–156.5°. The identity of these products obtained

from methyl cyanoquinolcarboxylate with those obtained from dicyanoquinol by Thiele and Günther, leads the author to propose the annexed formula for the product examined by him.



Ethyl *p*-benzoquinonecarboxylate is prepared by a method similar to that adopted for the methyl ester. Its isolation is more difficult, however, since it melts slightly above the ordinary

temperature and readily decomposes when in the liquid state. It forms yellowish-red leaflets, m. p. 22° , which decompose when preserved even at a low temperature. With aniline in ethereal solution, it yields *ethyl dianilino-p-benzoquinonecarboxylate*, dark red, almost black needles, m. p. $178-179^{\circ}$. H. W.

Action of Bromine on Aliphatic-Aromatic Compounds. HUGO BAUER and GUSTAV ENDRES (*J. pr. Chem.*, 1913, [ii], 87, 545-552).—An account of the action of bromine on *o*- and *p*-benzylbenzoic acids, phenylphthalide, homophthalic acid, phthalidecarboxylic acid and di-*p*-nitrodiphenylmethane.

p-Benzylbenzoic acid reacts with bromine in the cold yielding a *tribromo*-derivative, which crystallises in slender scales, m. p. $218-220^{\circ}$. When heated with bromine for three or four hours in a sealed tube at $110-120^{\circ}$, it gives rise to *dibromotetraphenylethylendi-p-carboxylic acid*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}_2\text{H}$, m. p. $260-262^{\circ}$.

α -Phenylphthalide and bromine at 120° yields the dilactone of dihydroxytetraphenylethanecarboxylic acid (Ullmann, A., 1896, i, 563), which is also obtained from *o*-benzylbenzoic acid at $110-120^{\circ}$. If the action of bromine on *o*-benzylbenzoic acid is carried out at the ordinary temperature, the lactone is accompanied by a *bromo-o-benzylbenzoic acid*, m. p. 137° .

Phthalidecarboxylic acid, $\text{CO}\langle\text{C}_6\text{H}_4\rangle\text{CH}\cdot\text{CO}_2\text{H}$, and bromine at 120° yield hydrogen bromide, carbon dioxide, and phthalic anhydride; the same products are also obtained from homophthalic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

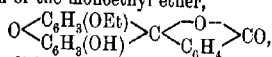
From the product of the action of bromine on di-*p*-nitrodiphenylmethane, only di-*p*-nitrobenzophenone could be isolated. F. B.

Hydrogenation of Santonic Acid. A Dihydrosantonin. II. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 711-714. Compare this vol., i, 730).—The author discusses the question of the constitution of santonin in the light of the results obtained by himself and other recent workers, and points out that the production of a dihydrosantonin cannot be reconciled with the views of Wienthaus and von Oettingen (this vol., i, 474).

Dihydrosantonin, $\text{C}_{15}\text{H}_{20}\text{O}_3$, crystallises in long prisms, m. p. 99° (*loc. cit.*), and has $[\alpha]_D^{25} + 75.19^{\circ}$ in 1.463% alcoholic solution. Its osime, $\text{C}_{15}\text{H}_{21}\text{O}_3\text{N}$, forms tufts of colourless prisms, m. p. about 235° . The semicarbazone crystallises in colourless prisms, m. p. 243° . R. V. S.

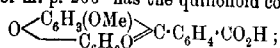
Constitution of Santonin. ANGELO ANGELI (*Ber.*, 1913, 46, 2233-2235).—The author points out that Asahina (this vol., i, 731), has overlooked the work of Angeli and Marino (A., 1907, i, 321) on the oxidation of santonin to heptanetetracarboxylic acid, the formation of which led them to the conclusion that santonin contains a bridged ring. F. B.

The Ethers and Esters of Fluorescein. HANS VON LIEBIG (*J. pr. Chem.*, 1913, [ii], 88, 26—48).—In previous papers (A., 1912, i, 376; this vol., i, 79) the author has described four monomethyl ethers and esters of fluorescein, a strongly yellow form of m. p. 266°, two pale yellow ethers of m. p. 265° (corresponding with Fischer and Hepp's [A., 1895, i, 291] ether of m. p. 262°) and 272°, and also a colourless ether of m. p. 256—257°, obtained by hydrolysing the dimethyl ether of m. p. 208° with ethyl alcoholic potassium hydroxide. It is now found that, during the hydrolysis, part of the methyl is replaced by ethyl, so that the colourless ether of m. p. 256—257° really consists of the lactone form of the monoethyl ether,



which, in a pure condition, crystallises in white prisms, m. p. 253—254°.

If the hydrolysis is carried out with methyl alcoholic potassium hydroxide, the colourless monomethyl ether of m. p. 272° is obtained. This ether represents the lactone form of the monomethyl ether, whilst the yellow ether of m. p. 266° has the quinonoid constitution



the ether of m. p. 265° (or 262°) is either a mixture or, more probably, a polymeric form similar to the quadrimolecular monomethyl ether described previously.

The monomethyl ester, obtained by warming fluorescein with methyl alcohol and sulphuric acid, has m. p. 282—283°, and not 252° as given by Feuerstein and Wallach (A., 1901, i, 723); the corresponding monomethyl ester has m. p. 251—252°, and not 242°.

By methylating the monomethyl ester of fluorescein with methyl sulphate, Kehrman and Dengler (A., 1909, i, 249) obtained a red compound of m. p. 176—177°, which they considered to be the methyl ester of the monomethyl ether of fluorescein. The author finds, however, that the product of the action consists of a mixture of the dimethyl ether of m. p. 198° (Kehrman's 3:6-dimethoxyfluorans) and Fischer and Hepp's (*loc. cit.*) coloured dimethyl ether of m. p. 208°.

When the dimethyl ether of m. p. 198° is heated with methyl alcohol and concentrated hydrochloric acid, and the resulting solution diluted with water and saturated with sodium chloride, a *hydrochloride* of the trimethyl ether of fluorescein is obtained, which, after precipitation from alcoholic solution by means of ether, has the composition $4\text{C}_{23}\text{H}_{20}\text{O}_5 \cdot 5\text{HCl} \cdot 10\text{H}_2\text{O}$ (compare Kehrman and Schennert, A., 1912, i, 1034); the addition of concentrated hydrochloric acid to a warm aqueous solution of this chloride causes the precipitation of a *chloride* of the composition $2\text{C}_{28}\text{H}_{19}\text{O}_5 \cdot 3\text{HCl} \cdot 8\text{H}_2\text{O}$, crystallising in stout, orange prisms having a bluish glance. The *sulphate* of the trimethyl ether of fluorescein is prepared by heating the dimethyl ether of m. p. 198° with methyl alcohol and sulphuric acid; it has m. p. 226°.

That the above salts are derivatives of the trimethyl ether to fluorescein has been established by reducing the sulphate with zinc dust and glacial acetic acid, when the trimethyl ether of fluorescein

was obtained, identical with that previously prepared by the direct methylation of fluorescein with methyl sulphate.

Oxidation of the trimethyl ether of fluorescein by means of lead dioxide in hot glacial acetic acid solution gives rise to the dimethyl ether of fluorescein, having m. p. 198° , and the above-mentioned trimethyl ether of fluorescein, which was isolated in the form of its nitrate, $C_{23}H_{18}O_5 \cdot HNO_3$, crystallising in light yellow leaflets.

Hydrolysis of the trimethyl ether of fluorescein with alcoholic potassium hydroxide leads to the formation of the dimethyl ether of fluorescein, $C_{22}H_{16}O_5$, which crystallises from alcohol in white needles, m. p. $204-205^{\circ}$, and is also obtained, together with the trimethyl ether, by methylating fluorescein with aqueous potassium hydroxide and methyl sulphate.

When oxidised by means of lead dioxide in hot glacial acetic acid solution the dimethyl ether of fluorescein yields the dimethyl ether of fluorescein of m. p. 198° .

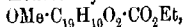
The monomethyl ether of fluorescein of m. p. 265° forms a potassium salt, $C_{21}H_{13}O_5K \cdot C_{22}H_{15}O_5K_2 \cdot 4H_2O$.

When heated with ethyl iodide and alcoholic potassium hydroxide, fluorescein yields a quadrimolecular monoethyl ether of the composition $3C_{20}H_{12}O_5 \cdot C_{22}H_{16}O_5 \cdot H_2O$, m. p. $330-331^{\circ}$, in addition to the diethyl ethers of m. p. 159° and 181° .

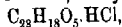
When esterified with methyl alcohol and sulphuric acid the monomethyl ethers of fluorescein of m. p. 265° , 266° , and 272° are converted into the dimethyl ether-ester of m. p. 208° , $OMe \cdot C_{19}H_{10}O_2 \cdot CO_2Me$, which crystallises in orange-yellow needles or dark red prisms, and is precipitated in the form of its sulphate, $2C_{22}H_{16}O_5 \cdot H_2SO_4 \cdot H_2O$, dark red, prismatic crystals (decomp. 140°) by the addition of water to the product of the esterification.

If, after esterification, the mixture is treated with aqueous sodium hydroxide and the precipitated ester purified by conversion into the hydrochloride, $C_{22}H_{16}O_5 \cdot HCl \cdot 2H_2O$, a second modification of the dimethyl ether-ester is obtained; this crystallises in yellowish-red prisms, m. p. 195° , and on repeated crystallisation from ethyl acetate is transformed into the dimethyl ether of m. p. 208° .

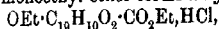
The ethyl ester of the monomethyl ether of fluorescein,



prepared by esterifying the monomethyl ether with ethyl alcohol and sulphuric acid, has m. p. $194-195^{\circ}$, and yields a hydrochloride,



crystallising in yellowish-red needles; the methyl ester of the monoethyl ether of fluorescein, $OEt \cdot C_{19}H_{10}O_2 \cdot CO_2Me$, obtained in a similar manner, crystallises in yellowish-red prisms or needles, m. p. 216° ; the ethyl ester of the monoethyl ether forms a hydrochloride,

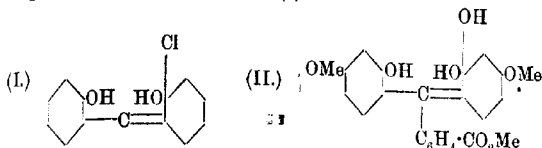


crystallising in yellowish-red needles.

A solution of the sulphate of the monomethyl ester of fluorescein (m. p. $282-283^{\circ}$) in sodium hydrogen carbonate deposits a sodium salt of the composition $C_{21}H_{14}O_5 \cdot NaHSO_4$ as a fine red powder.

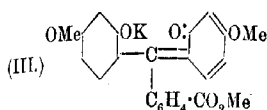
According to the author (A., 1912, i, 381), the salts of fluorescein and its ethers with acids owe their solubility in water to the rupture

of the oxygen bridge of the pyrone ring and formation of compounds having the structure represented in (I).



If this view is correct the salts of the trimethyl ether of fluorescein should give rise on hydrolysis to the compound (II), which with

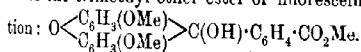
potassium hydroxide would form a quinonoid having the annexed formula (III), and, from analogy with the quinonoid salts of quinolphthalein and 4:5-dinitrofluorescein (this vol., i, 80); compare also



Baeyer, A., 1910, i, 249), this salt should have a blue colour.

Such an *o*-quinonoid *potassium* salt has been prepared by triturating the trimethyl ether of fluorescein with 33% aqueous potassium hydroxide. It has the composition $C_{23}H_{19}O_6K \cdot H_2O$, and rapidly decomposes when kept, yielding a brown substance, which has m. p. about 120° , with previous sintering, and dissolves in methyl and ethyl alcohols, yielding solutions coloured respectively pure green and brownish olive-green; from these solutions the addition of alkalis causes the separation of the dimethyl ether of fluorescein.

When freshly prepared and treated with water, the blue potassium salt partly dissolves with the formation of a deep blue solution, from which acetic acid precipitates a *hydrate* of the trimethyl ether-ester of fluorescein, $C_{23}H_{20}O_6 \cdot H_2O$, in yellow flocks. This melts and loses water at 173° . It dissolves in alkali hydroxides with a blue colour, and is, therefore, considered to be the parent substance of the blue potassium salt. On treatment with water, the greater part of the blue potassium salt is converted into an insoluble brown substance, which crystallises in needles, is insoluble in alkalis, and probably represents the trimethyl ether-ester of fluorescein of the following constitution:



F. B.

[Fluorescein.] HANS VON LIEBIG (*J. pr. Chem.*, 1913, [ii], 88, 96).—A correction. Owing to an error in the thermometer the m. p.'s of a number of ethers and esters of fluorescein recorded in previous papers (A., 1912, i, 376; this vol., i, 79) are too high.

The lactone form of the monomethyl ether has m. p. 266° (not 273°), the quinonoid form 259° (not 266°), and the monomethyl ester m. p. 274 — 275° (not 283°). The lactone form of the monomethyl ether, previously described as melting at 253 — 254° , has m. p. 247 — 248° . The monoethyl ester has m. p. 247° .

F. B.

Fluorescein Methyl Ethers. OTTO FISCHER and EDUARD HEPF (*Ber.*, 1913, 46, 1951—1959. Compare A., 1895, i, 291).—A reply to

von Liebig (this vol., i, 79) and to Kehrman and Dengler (A., 1909, i, 249). The divergence of the results of these workers from those previously obtained by the authors is probably to be attributed to impure fluorescein. The fluorescein used by the authors was always previously purified through the diacetyl derivative.

Methylation of purified fluorescein by methyl iodide and alcoholic potassium hydroxide gives as main product the orange-red dimethyl ether, m. p. 208°, together with a little of the colourless lactonic dimethyl derivative, m. p. 197—198°, which previously escaped detection. A similar result is obtained by the application of diazomethane in nitrobenzene solution. Fluorescein monomethyl ester, m. p. 282°, obtained by the interaction of fluorescein and methyl alcohol in the presence of sulphuric acid or hydrogen chloride, also gives a similar product to the above whether further methylated in methyl alcohol by methyl iodide and potassium hydroxide or in nitrobenzene solution by methyl sulphate. In the latter case no indication whatever of a substance, m. p. 176—177° (Kehrman and Dengler, *loc. cit.*), was observed.

By hydrolysis of fluorescein dimethyl ether, m. p. 208°, with methyl. alcoholic potassium hydroxide, the colourless lactonic fluorescein monomethyl ether, m. p. 265—266°, can be obtained; on methylation of this by methyl sulphate in nitrobenzene solution the chief product is the dimethyl ether, m. p. 197—198°. D. F. T.

Substituted Crotonolactoneacetic [α -Monolactones of γ -Hydroxydihydromuconic] Acids. ERICH BESCHKE [with GEORG KÖHRES and F. MARSHALL] (*Annalen*, 1913, 398, 265—298).—The interaction of phenanthraquinone, ethyl bromoacetate, and zinc in boiling benzene leads to the formation of γ -hydroxy- β - γ -diphenylene-

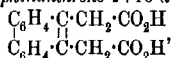
Δ^* -dihydromuconic acid α -lactone, $\text{C}_6\text{H}_4\cdot\text{C}(\text{CH}_2\cdot\text{CO}_2\text{H})\cdot\text{O}$
 $\text{C}_6\text{H}_4\cdot\text{C}=\text{CH}\text{CO}$, m. p.

216°, colourless crystals, which exhibits considerable stability towards dilute alkaline potassium permanganate, zinc dust and acetic acid, and bromine. Its sodium salt, $\text{C}_{18}\text{H}_{11}\text{O}_4\text{Na}$, reacts with aqueous bromine to form, after acidification, α -bromo- γ -hydroxy- β - γ -diphenylene- Δ^* -dihydromuconic acid α -lactone, $\text{C}_{18}\text{H}_{11}\text{O}_4\text{Br}$, m. p. 198°, by the reduction of which by zinc dust and alcohol the original acid is regenerated.

The addition of saturated aqueous sodium hydroxide to a boiling alcohol solution of γ -hydroxy- β - γ -diphenylene- Δ^* -dihydromuconic acid α -lactone yields sodium γ -hydroxy- β - γ -diphenylene- Δ^* -dihydromuconate, $\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$

, an aqueous solution of which is reduced by

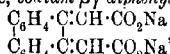
3% sodium amalgam to phenanthrene-9:10-diacetic acid,



m. p. 305°, colourless crystals. This acid forms an ethyl ester, $\text{C}_{22}\text{H}_{22}\text{O}_4$, m. p. 94°, and is converted by heating into 2-ketophenanth-

hydrindene, $\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{CH}_2\text{CO}$, m. p. 219°, colourless leaflets (oxime, m. p. 258° [decomp.])

γ -Hydroxy- β -diphenylene- Δ^2 -dihydromuconic acid α -lactone forms an *ethyl ester*, $C_{20}H_{16}O_4$, m. p. 104° , from which the acid is regenerated by hydrolysis with acids. However, when a cold alcoholic suspension of the ester is treated with sodium ethoxide and the resulting yellow solution is acidified, *ethyl hydrogen β -diphenylenemuconate*, $C_6H_4 \cdot C \cdot CH \cdot CO_2Et$, is obtained as a viscous, yellow mass which by keeping or warming changes to the *ethyl ester*, m. p. 234° , colourless crystals, of the $\alpha\delta$ -lactone of δ -hydroxy- β -diphenylene- Δ^2 -dihydromuconic acid, $C_6H_4 \cdot CH \cdot CH(CO_2Et) \cdot CO$, m. p. 289° (decomp.), colourless crystals. By treating a boiling alcoholic solution of ethyl γ -hydroxy- β -diphenylene- Δ^2 -dihydromuconic acid α -lactone with concentrated aqueous sodium hydroxide, *sodium- β -diphenylenemuconate*,



is obtained, from which a yellow acid is obtained by acidification; by recrystallisation the yellow acid, *β -diphenylenemuconic acid*, is changed into the lactone, m. p. 280° (decomp.), of δ -hydroxy- β -diphenylene- Δ^2 -dihydromuconic acid. An aqueous alkaline solution of β -diphenylenemuconic acid is reduced by sodium amalgam to phenanthrene-9:10-diacetic acid, from which phenanthraquinone is obtained by oxidation with chromic and acetic acids.

By oxidation with chromic and acetic acids at 75° and finally at 90° , the lactone of δ -hydroxy- β -diphenylene- Δ^2 -dihydromuconic acid is converted into the lactone, $C_6H_4 \cdot CH \cdot CH_2 \cdot O$, m. p. 211° , colourless crystals, which forms a *phenylhydrazone*, $C_{23}H_{18}O_2N_2$, m. p. 234° , faintly yellow leaflets, and *o-aminoanilino* derivative, $C_{23}H_{18}O_2N_2$, m. p. 236° , with *o*-phenylenediamine, and is oxidised by chromic acid in boiling glacial acetic acid to the lactone, $C_6H_4 \cdot C \cdot CH_2 \cdot O$, m. p. 302° , yellow crystals. The latter lactone, which is more conveniently obtained directly by the oxidation of the lactone of δ -hydroxy- β -diphenylene- Δ^2 -dihydromuconic acid, forms a *phenylhydrazone*, m. p. 292° , yellow needles, *anilino*-derivative, $C_{23}H_{18}O_2N_2$, m. p. 263° , yellow needles, *o-aminoanilino*-derivative, m. p. 269° (decomp.), and *phenazine*, $C_{22}H_{14}ON_2$, m. p. 271° , yellowish-red needles.

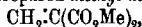
C. S.

Synthesis of Derivatives of dicyclo-[1,3,3]-Nonane. I. HANS MEERWEIN and WILHELM SCHÜRMANN (*Annalen*, 1913, 398, 196—242).

—Derivatives of dicyclo-[1:3:3]-nonane (annexed formula) have been prepared from formaldehyde and ethyl malonate by a very simple and smooth reaction.

$\begin{array}{c} CH_2 \cdot CH \cdot CH_2 \\ | \quad | \quad | \\ CH_2 \cdot CH_2 \cdot CH_2 \\ | \quad | \quad | \\ CH_2 \cdot CH \cdot CH_2 \end{array}$ Perkin, in conjunction with Haworth (T., 1898, 73, 330) and Bottomley (T., 1900, 74, 294), has shown that formaldehyde and malonic esters condense to form, under different conditions, methylenemalonic esters, methylenebis-malonic esters, or pentane- $\alpha\gamma\gamma\gamma$ -hexacarboxylic esters. By this

method the authors have prepared *methyl methylenemalonate*,

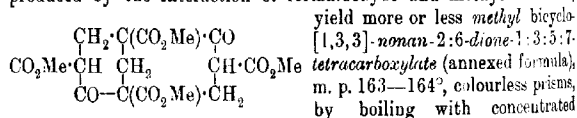


as a mixture, b. p. 150—180°/15 mm, of the uni- and bi-molecular forms (the latter is an amorphous, white powder which is depolymerised by distillation at 200—203°), and also *methyl pentane-α,γ,εε-hexacarboxylate*, $\text{CH}(\text{CO}_2\text{Me})_2 \cdot \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{Me})_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Me})_2$, m. p. 62—63°, hard, colourless prisms. The latter, which can also be obtained by the interaction of methyl methylenebismalonate and methyl methylenemalonate in alcoholic sodium methoxide at the ordinary temperature, is converted by boiling methyl alcoholic sodium methoxide into methyl carbonate and *methyl cyclohexan-1-one-2:4:4:6-tetracarboxylate*, $\text{CO} < \begin{matrix} \text{CH}(\text{CO}_2\text{Me}) \cdot \text{CH}_2 \\ \text{CH}(\text{CO}_2\text{Me}) \cdot \text{CH}_2 \end{matrix} > \text{C}(\text{CO}_2\text{Me})_2$, m. p. 121—122°, colour-

less, rhombic prisms, methyl *bicyclo-[1,3,3]-nonane-2:6-dione-1:3:5:7-tetracarboxylate* (see below) being also formed. Methyl *cyclohexan-1-one-2:4:4:6-tetracarboxylate* exists as the ketonic modification in the solid state, but is rapidly enolised by alcohol, the solution in this solvent producing a reddish-violet coloration with ferric chloride. By acidifying a solution of the ester in alcoholic sodium methoxide, the enol is precipitated as a viscous oil, the ethereal solution of which deposits almost quantitatively the ketonic modification after a short time. This property of rapidly ketonising is utilised to separate the ester from the accompanying *dicyclononanedione-tetracarboxylate*.

By heating with half volume of water at 200° for thirty minutes (compare following extract), methyl *cyclohexan-1-one-2:4:4:6-tetracarboxylate* undergoes the ketonic decomposition and yields *methyl cyclohexan-1-one-4:4-dicarboxylate*, b. p. 160—161°/14 mm, which has no acid properties, does not give a coloration with ferric chloride, forms a *semicarbazone*, m. p. 190° (decomp.), and *dicinnamylidene* derivative, $\text{C}_{28}\text{H}_{26}\text{O}_3$, m. p. 186°, yellow needles dissolving to a blue solution in concentrated sulphuric acid, and yields Perkin's *cyclohexan-1-one-4-carboxylic acid* (T., 1904, 85, 424; 1906, 89, 1648) by hydrolysis.

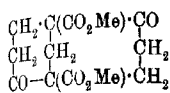
All the substances, namely, methyl methylenemalonate and methyl methylenebismalonate, and methyl pentane-α,γ,εε-hexacarboxylate, produced by the interaction of formaldehyde and methyl malonate,



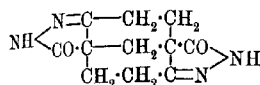
methyl-alcoholic sodium methoxide, the best yield being obtained by using methyl methylenebismalonate (1 mol.) and methyl methylenemalonate (2 mols.).

The constitution of the *dicyclononane* derivative, which can also be prepared by heating methyl malonate (4 mols.) and methylene iodide (3 mols.), or methyl *cyclohexan-1-one-2:4:4:6-tetracarboxylate* and methyl methylenemalonate, with methyl alcoholic sodium methoxide, is proved, not only by the preceding method of preparation, but also by the following reactions.

Methyl *dicyclo*-[1,3,3]-nonan-2:6-dione-1:3:5:7-tetracarboxylate develops a reddish-violet coloration with alcoholic ferric chloride, forms a pale green *copper* derivative and a crystalline *disodium* derivative, $C_{17}H_{18}O_{10}Na_2$, and possesses pronounced acid properties,



indicating that the substance is a cyclic β -ketonic ester. By heating with water at 170–180°, it is converted quantitatively into methyl *dicyclo*-[1,3,3]-nonan-2:6-dione-1:5-dicarboxylate (annexed formula), m. p. 187–188°, colourless prisms or quadratic plates. This ester is insoluble in alkalis and does not develop a coloration with ferric chloride. However, it still contains two β -ketonic groups because it reacts with hydrazine hydrate and with phenylhydrazine in glacial acetic acid to form respectively the *dipyrzalone* (annexed formula), m. p. 300° (decomp.), colourless prisms, and corresponding *diphenyldipyrzalone*, m. p. 270°, pale yellow leaflets.



prisms, and corresponding *diphenyldipyrzalone*, m. p. 270°, pale yellow leaflets.

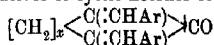
The decomposition of methyl *dicyclo*-[1,3,3]-nonan-2:6-dione-1:3:5:7-tetracarboxylate by dilute alkali hydroxide is too profound to be of any service, but by hydrolysis by aqueous barium hydroxide at 105° and acidification of the resulting barium salt, the ester yields 3:7-dimethyl 1:5-dihydrogen *dicyclo*-[1,3,3]-nonan-2:6-dione-1:3:5:7-tetracarboxylate, m. p. 205–207° (decomp.), small prisms or needles, which gives a violet coloration with ferric chloride, regenerates the original ester, m. p. 163–164°, by treatment of its silver salt with methyl iodide, and is converted by heating into methyl *dicyclo*-[1,3,3]-nonan-2:6-dione-3:7-dicarboxylate, $C_{13}H_{16}O_6$, m. p. 136–137°, colourless prisms. The latter is soluble in alkalis, develops a reddish-violet coloration with ferric chloride, and forms a *dipyrzalone*, $C_{11}H_{12}O_2N_4$, decomp. above 300°, and *diphenyldipyrzalone*, $C_{23}H_{20}O_2N_4$, decomp. above 300°, thus indicating that the original *dicyclononane* derivative,

methyl *dicyclo*-[1,3,3]-nonan-2:6-dione-1:3:5:7-tetracarboxylate, must contain four β -keto-groups.

$\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CO} \\ | \quad | \\ \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \\ | \quad | \quad | \\ \text{CO} \cdot \text{CH} \cdot \text{CH}_2 \end{array}$ *dicyclo*-[1,3,3]-Nonan-2:6-dione (annexed formula), m. p. 141°, b. p. 180°/20 mm., rhombic prisms, is

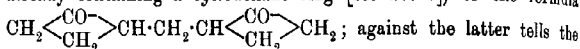
obtained in about 34% yield by boiling methyl *dicyclononanedi*onetetracarboxylate or methyl *dicyclononanedi*one-1:5-dicarboxylate with dilute hydrochloric acid, or quantitatively by heating 3:7-dimethyl 1:5-dihydrogen *dicyclononanedi*onetetracarboxylate, or methyl *dicyclononanedi*one-3:7-dicarboxylate with water at 200°. *Dicyclononanedi*one is volatile with steam, forms a *diphenylhydrazone*, $C_{21}H_{24}N_4$, and a *di-oxime*, $C_9H_{14}O_2N_2$, m. p. 205–206° (decomp.), regular octahedra, and is stable to potassium permanganate, these reactions indicating that the substance is a dicyclic diketone. It condenses very readily with alcoholic benzaldehyde, or cinnamaldehyde in the presence of a little concentrated sodium hydroxide, yielding 3:7-dibenzylidenedicyclo-[1,3,3]-nonan-2:6-dione, $C_{25}H_{30}O_2$, m. p. 201°, faintly yellow needles, and the *dicinnamylidene* derivative, $C_{27}H_{34}O_2$, m. p. 246°, pale yellow powder, which dissolve in concentrated

sulphuric acid with a pale yellow and orange-red colour respectively. The significance of these slight colorations is important, because Wallach, Stobbe, and others have shown that the dibenzylidene and dicycnamylidene derivatives of cyclic ketones of the type



develop intensely yellow and violet colorations respectively with concentrated sulphuric acid. Hence the inference is drawn that only one methylene group is attached directly to a carboxyl group in the *dicyclononanedione*.

The oxidation of *dicyclononanedione* by warm nitric acid, D 1.2, yields Guthzeit and Engelmann's pentane- $\alpha\beta\delta\epsilon$ -tetracarboxylic acid (*anhydride*, $\text{C}_9\text{H}_8\text{O}_8$, m. p. 161° ; *methyl ester*, $\text{C}_{12}\text{H}_{20}\text{O}_8$, m. p. 60° , b. p. $210^\circ/20$ mm.). The formation of this acid proves that the diketone must have either the formula assigned to it by the authors (which is proved by the formation of methyl *dicyclononanedione* tetra-carboxylate, and therefore indirectly of the diketone, from a substance already containing a *cyclohexane* ring [see above]) or the formula



against the latter tells the fact that the formation of a *cyclobutane* derivative has never been observed when there is a possibility for the reaction to produce a *cyclohexane* derivative.

C. S.

Quantitative Investigation of the Photochemical Transformation of *o*-Nitrobenzaldehyde into *o*-Nitrosobenzoic Acid. FRITZ WEIGERT and LUDWIG KUMMERER (*Ber.*, 1913, 46, 1884—1885. Compare this vol., ii, 370; Kailan, *ibid.*, i, 51, 733).—A further criticism of Kailan's work on this subject.

F. B.

Quantitative Investigation of the Photochemical Transformation of *o*-Nitrobenzaldehyde into *o*-Nitrosobenzoic Acid. II. ANTON KAILAN (*Ber.*, 1913, 46, 2175—2179. Compare this vol., i, 51).—In reply to Weigert and Kummerer's criticism (this vol., ii, 370) that the titration of *o*-nitrosobenzoic acid using phenolphthalein is not trustworthy in presence of much *o*-nitrobenzaldehyde, the author shows that the method gives satisfactory results.

J. C. W.

Bromination of Certain Ketones and of Some Secondary Hydroaromatic Alcohols. FERNAND BODROUX and FELIX TAPPORET (*Compt. rend.*, 1913, 156, 1840—1841. Compare A., 1912, i, 567).—Bromination was effected by the addition of a solution of the ketone or alcohol in carbon tetrachloride to an excess of bromine dissolved in the same solvent. After six hours, excess of bromine and carbon tetrachloride were removed by means of a current of air.

1-Methyl-2-cyclohexanone yielded *tetrabromomethylcyclohexanone*, small, white needles, m. p. $105-107^\circ$, together with a small quantity of a mixture of tribromomethylcyclohexanones which could not be separated from one another. 1-Methyl-2-cyclohexanol gave a poor yield of a mixture of tribromomethylcyclohexanones.

1-Methyl-3-cyclohexanone was practically quantitatively converted

into a tribromomethylcyclohexanone. The latter was very difficult to purify, but had m. p. 55—58°.

1-Methyl-4-cyclohexanone yielded a *tetrabromo*-derivative, white needles, m. p. 79°. The same substance was obtained from 1-methyl-4-cyclohexanol.

1:3-Dimethyl-4-cyclohexanone gave a *tetrabromo*-derivative, white prisms, m. p. 62—63°.

The bromo-derivatives of the homologues of cyclohexanone are somewhat unstable. At temperatures slightly above their m. p.'s, they are decomposed into bromine, hydrogen bromide, and bromo-phenols. The same transformation occurs slowly at the ordinary temperature under the influence of light.

H. W.

Catalytic Hydrogenation of the Two Methylcyclopentanones.

MARCEL GODCHOT and FELIX TABOURY (*Bull. Soc. chim.*, 1913, [iv], 13, 591—599).—It is shown that the reduction of the methylcyclopentanones by Sabatier and Senderens' method is quite analogous to that of cyclopentanone (A., 1911, i, 385; 1912, i, 34), the products being the corresponding methylcyclopentanols and dimethylcyclopentylcyclopentanones, the latter predominating (compare Zelinsky, A., 1911, i, 988).

1-Methylcyclopentan-3-one yields 1-methylcyclopentan-3-ol (*phenylurethane*, m. p. 82°, colourless needles from alcohol) and 3-methylcyclopentyl-2-(or 3')-methylcyclopentan-5'-one (annexed formulæ), D_{16}^{25} 0.9365,

n_D^{25} 1.4700, b. p. 245°, a colourless liquid having an odour of menthol; it yields a *semicarbazone*, m. p. 137°, crystallising in needles, and with hydroxylamine a *product*, m. p. 75—100°, which is probably a mixture of two stereoisomeric oximes.

Attempts to prepare 1-methylcyclopentan-2-one by (1) the action of magnesium methyl iodide on 1-chlorocyclopentan-2-one and (2) the action of methyl iodide on cyclopentanone in presence of sodamide were unsuccessful; the second reaction yielded cyclopentylidene-3-methylcyclopentan-2-one, of which the *oxime*, m. p. 85°, colourless needles, and the *semicarbazone*, m. p. 193°, were prepared.

The 1-methylcyclopentan-2-one required was prepared by Bouveault's method (A., 1900, i, 171). On reduction by nickel at 150°, 1-methylcyclopentan-2-ol, D_{16}^{25} 0.9238, n_D^{25} 1.4466, b. p. 146—147° (*phenylurethane*, m. p. 84°), was obtained with 2-methylcyclopentyl-3-methylcyclopentan-2'-one as a principal product. The latter has D_{16}^{25} 0.9238, n_D^{25} 1.4724, b. p. 239—241°, and is a colourless liquid with an odour of menthol; it yields a *semicarbazone*, m. p. 202—203°, crystallising from alcohol in needles. Loof (A., 1894, i, 405) has already prepared a methylcyclopentanol, which may be identical with that described above.

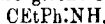
T. A. H.

Ketimines. CHARLES MOUREU and GEORGES MIGNONAC (*Compt. rend.*, 1913, 156, 1801—1806).—The authors have succeeded in

isolating a series of ketimines of the general formula $CR_2:NH$, the bromomagnesium derivatives of which are formed as intermediate products in the preparation of ketones by the action of Grignard's reagents on nitriles.

For the preparation of purely aromatic ketimines, the solid product of the action of the aryl-nitrile on the magnesium aryl haloid is brought, little by little, into a mixture of crushed ice and ammonium chloride, the mixture extracted with ether, the ethereal solution dried and saturated with dry hydrogen chloride. The precipitated imine-hydrochloride is filtered, suspended in ether, and decomposed by dry ammonia gas. After removal of ammonium chloride, the imine is obtained by evaporating the ethereal solution. Mixed fatty-aromatic ketimines are generally more readily decomposed by water, and their isolation is preferably effected by passing dry hydrogen chloride directly into the ethereal suspension of the magnesium derivative. The free imine is isolated from the hydrochloride so formed in the same manner as that adopted for aromatic ketimines.

Ketimines are generally oils or solids of low m. p. which yield crystalline salts. The hydrochlorides dissolve readily in chloroform, and are decomposed by water into the corresponding ketone and ammonium chloride. The free bases are much less sensitive to the action of water than the salts. Ketimines readily combine with bromine. They yield acyl derivatives which are decomposed by cold dilute hydrochloric acid with the formation of ketones. The constants of the following ketimines are given: *Phenyl ethyl ketimine*,



has b. p. $101.5-102.5/13.5$ mm., D_4^{20} 0.9902, n_D^{20} 1.5476. Its hydrochloride and acetyl derivative have m. p. 145° and 126° respectively. *Phenyl propyl ketimine*, has b. p. $99/8$ mm., D_4^{18} 0.9751, n_D^{18} 1.5333. *Phenyl isobutyl ketimine*, b. p. $113-114/12.5$ mm., D_4^{20} 0.9489, n_D^{20} 1.5270. *Phenyl cyclohexyl ketimine*, b. p. $135-138/5$ mm. *Diphenyl ketimine*, b. p. $127/3.5$ mm., D_4^{19} 1.0847, n_D^{19} 1.6191. *Phenyl o-tolyl ketimine*, b. p. $136-137/4$ mm., D_4^{25} 1.0614, n_D^{25} 1.6065. *Phenyl p-tolyl ketimine*, m. p. 37° , b. p. $147/5$ mm., D_4^{20} 1.0617, n_D^{20} 1.6097. *Phenyl a-naphthyl ketimine*, m. p. $68-69^\circ$, b. p. $181.5/4.5$ mm. H. W.

Catalytic Formation of Benzophenone by Calcium Carbonate. PAUL SABATIER (*Anal. Fis. Quim.*, 1913, 11, 274-275).—When the vapour of benzoic anhydride is passed over calcium carbonate at about 500° , benzene, benzophenone, and traces of anthraquinone are formed. G. L. J.

Transformation of 2:6-, 2:4'- and 2:4-Dibromobenzophenones into Bromofluorenones. PIETER J. MONTAGNE and JACOB MOLL VAN CHARANTE (*Rec. trav. chim.*, 1913, 32, 164-173. Compare A., 1910, i, 42).—When 2:6-, 2:4', or 2:4-dibromobenzophenone is heated, hydrogen bromide is evolved, and a bromofluorenone formed. Concurrently a certain amount of bromination occurs, due apparently to the hydrogen bromide evolved, and, since different by-products are obtained from 2:4'- and 2:4-dibromobenzophenone, it appears that it is the unchanged original substance which is thus affected.

8-Bromofluorenone, $\text{C}_6\text{H}_4\text{Br}-\text{CO}-\text{C}_6\text{H}_4$, m. p. 135° , b. p. ca. 395° (decomp.), is obtained when 2:6-dibromobenzophenone is heated at its b. p. during two to three days. On reduction by means of sodium amalgam in boiling alcoholic solution, it is converted into fluorenyl alcohol, m. p. 153° , whilst oxidation by concentrated sulphuric acid and mercuric sulphate transforms it into phthalic anhydride.

When 2:4'-dibromobenzophenone is heated, it yields a mixture of unchanged material and two substances which can be separated by sublimation under reduced pressure. At about $170-180^\circ$, 6-bromofluorenone is obtained. After recrystallisation from benzene, it forms needles and plates, m. p. 165.5° , or compact crystals, m. p. 162.5° . After re-solidification the latter melt at 165.5° . Reduction with sodium amalgam in boiling alcoholic solution transforms it into fluorenone, m. p. 82° , whilst, when oxidised with concentrated sulphuric acid and mercuric sulphate, it yields phthalic anhydride. The residue obtained from the sublimation of 6-bromofluorenone, when sublimed at about 225° , gives a dibromofluorenone, $\text{C}_{13}\text{H}_8\text{OBr}_2$, yellow crystals, m. p. $215.5-216^\circ$.

When 2:4-dibromobenzophenone is treated in the same manner as the 2:4'-isomeride, it yields 6-bromofluorenone. The residue left in the sublimation apparatus, after repeated crystallisations from benzene and alcohol, gives 6:8-dibromofluorenone, m. p. 225° . H. W.

$\alpha\beta$ -Unsaturated Diketones. OTTO DIELS and PETER SHARROFF (*Ber.*, 1913, 46, 1862—1870. Compare A., 1911, i, 464).—Under the influence of 33% aqueous potassium hydroxide, dimethyl diketone monoxime readily condenses with benzaldehyde, cinnamaldehyde and furfuraldehyde, yielding oximes of $\alpha\beta$ -unsaturated ketones of the formula $\text{CH}_3\text{CH}=\text{C}(\text{NOH})\cdot\text{C}(\text{OMe})_2$, from which the corresponding ketones cannot be obtained by any of the usual methods. The removal of the oximino-group may, however, be effected by distilling a mixture of the oxime with phthalic anhydride or succinic anhydride in superheated steam, but the yield of unsaturated diketone thus obtained is very small.

Styryl methyl diketone monoxime, $\text{CHPh}\cdot\text{CH}=\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{OMe})_2$, prepared from benzaldehyde and dimethyl diketone monoxime, crystallises from alcohol in long, colourless needles, m. p. 147° (corr.), and dissolves in aqueous alkali hydroxides, yielding yellow solutions; with 33% potassium hydroxide it forms a *potassium salt*. It is accompanied by an orange-yellow substance, probably

$\text{CHPh}[\text{CH}_2\cdot\text{CO}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CH}:\text{CHPh}]_2$,
m. p. $216-220^\circ$ (decomp.).

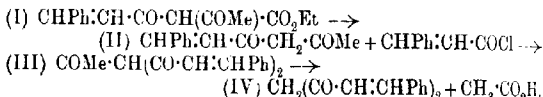
That the condensation of the aldehyde takes place at the methyl group adjacent to the oximino-group has been established by the conversion of the styryl methyl diketone monoxime by boiling with strong hydrochloric acid into 3-acetyl-5-phenyl-4:5-dihydroisoxazole, $\text{CHPh}\cdot\text{CH}=\text{O} \xrightarrow{\text{N}} \text{C}\cdot\text{C}(\text{OMe})$, which crystallises in stout prisms, m. p. $97-98^\circ$, and when warmed with aqueous potassium hydroxide is transformed into a substance, m. p. about 254° (decomp.).

On treatment with oxalyl chloride in ethereal solution the oxime yields a compound, $\text{CHPh}\cdot\text{CH}\cdot\text{C}(\text{COMe})\cdot\text{N}\cdot\text{O}\cdot\text{COCl}$, which crystallises in colourless needles, m. p. 59° , and is decomposed by water with the formation of cinnamic acid. The dibromide of styryl methyl diketone forms yellow crystals, m. p. 86° , and slowly decomposes when kept.

Cinnamylidenediacetyl monoxime (β -styrylvinylyl methyl diketone monoxime), $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{COMe}$, crystallises in slender, yellow needles, m. p. 148° , which become strongly electric when rubbed, give an intense purple-red coloration with sulphuric acid, and on distillation with phthalic anhydride in superheated steam yield cinnamylidenediacetyl, brownish-yellow needles, m. p. 49° .

Furfurylidenediacetyl monoxime (β -furfurylvinylyl methyl diketone monoxime), $\text{C}_4\text{H}_3\text{O}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{COMe}$, has m. p. 132° , and with strong aqueous potassium hydroxide yields a potassium salt. F. B.

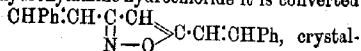
Curcumin. VICTOR LAMPE and J. MIŁOBĘDZKA (*Ber.*, 1913, 46, 2235—2240).—The authors are endeavouring to confirm, by direct synthesis, the formula, $\text{CH}_2[\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{OH}]_2$, proposed for curcumin by Miłobędzka, Kostanecki, and Lampe (*A.*, 1910, i, 628), and with this object in view have first of all turned their attention to the preparation of the parent substance, dicinnamoylmethane (IV), the synthesis of which was finally accomplished from ethyl cinnamoylacetoacetate by the method indicated in the following scheme :



Cinnamoylaceton (II), prepared by hydrolysis and simultaneous elimination of carbon dioxide from ethyl cinnamoylacetoacetate (I), crystallises in yellow prisms, m. p. 86 — 88° , and develops a yellowish-green coloration with sulphuric acid. Its alcoholic solution gives with copper acetate a green precipitate, and with ferric chloride a deep red coloration. When boiled with hydroxylamine hydrochloride in alcoholic solution, it is converted into 3(or 5)-styryl-5(or 3)-methylisooxazole, $\begin{array}{c} \text{CMe}\cdot\text{CH} \\ \text{O} \text{---} \text{N} \end{array} \text{C}\cdot\text{CH}\cdot\text{CHPh}$ or $\begin{array}{c} \text{CMe}\cdot\text{CH} \\ \text{N} \text{---} \text{O} \end{array} \text{C}\cdot\text{CH}\cdot\text{CHPh}$, which crystallises in white leaflets, m. p. 92 — 94° . On successive treatment with sodamide and cinnamoyl chloride in ethereal solution, it yields dicinnamoylaceton (III). This has m. p. 112 — 114° , gives the same reactions as cinnamoylaceton with cupric acetate and ferric chloride, and yields strongly yellow, fluorescent solutions with sulphuric acid.

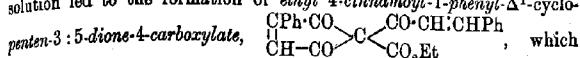
Dicinnamoylmethane (IV), prepared by boiling dicinnamoylaceton with 50% acetic acid, crystallises in bronze-yellow, prismatic needles, m. p. 144° . In its chemical properties it strongly resembles curcumin. Thus, it dyes cotton a pale yellow without a mordant, dissolves in sulphuric acid, yielding an orange-red solution having a yellow fluor-

essence, and gives with copper acetate and ferric chloride in alcoholic solution a green precipitate and a deep red coloration respectively. When boiled with alcoholic hydroxylamine hydrochloride it is converted into 3:5-distyrylisooxazole,

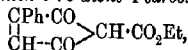


lising in almost colourless, prismatic needles, m. p. 170—172°.

Attempts to prepare ethyl dicinnamoylmalonate by the successive action of sodium and cinnamoyl chloride on ethyl malonate in ethereal solution led to the formation of ethyl 4-cinnamoyl-1-phenyl- Δ^1 -cyclopenten-3:5-dione-4-carboxylate,

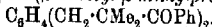


forms prismatic needles, m. p. 188—189°, and is accompanied by ethyl 1-phenyl- Δ^1 -cyclopenten-3:5-dione-4-carboxylate,

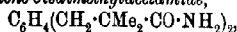


This crystallises in prismatic needles, m. p. 107—109°, and yields deep red alcoholic solutions. F. B.

Diketones Obtained by the Action of Xylene Dibromides on the Sodium Derivative of Phenyl *iso*Propyl Ketone, and their Decomposition by Sodamide. PH. DUMESNIL (*Compt. rend.*, 1913, 157, 53—55. Compare A., 1911, i, 719, and Haller and Bauer, A., 1911, i, 726).—*o*-, *m*-, and *p*-Xylene dibromides react with the sodium derivative of phenyl *iso*propyl ketone in benzene solution to give the corresponding bis-(β -benzoyl- β -methylpropyl)benzenes,



The *ortho*-derivative is obtained as small, colourless crystals, m. p. 68°, giving a *dioxime*, m. p. 240°; the *meta* in large, colourless crystals, m. p. 44°, giving a *dioxime*, m. p. 210°, and the *para* in colourless needles, m. p. 113°, yielding a *dioxime*, m. p. 278°. All three of these diketones are decomposed, by warming them with sodamide in xylene solution, into the corresponding bis-dimethylacetamides. *o*-Xylene-bisdimethylacetamide,



is a colourless, crystalline solid, m. p. 130°; the *meta*-isomeride, colourless needles, m. p. 162°; and the *para*-isomeride, m. p. 238°. They are all hydrolysed by heating with 50% sulphuric acid in sealed tubes for six hours at 150° to the corresponding *acids* having respectively m. p.'s 135°, 155°, and 217°. W. G.

Di-iminonaphthol Hydrochlorides. III. OSWALD MILLER (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 580—608. Compare A., 1911, i, 308, 465).—When crystallised from water and from alcohol, di-iminonaphthol hydrochloride shows different solubilities in 50% aqueous alcohol. Further, whilst hydration in neutral aqueous solution of the salt obtained from water gives yields of amino- α -naphthaquinone varying regularly with the temperature, the hydrochloride separated from alcohol always yields smaller and inconstant proportions of the quinone owing to the simultaneous formation of a third amino naphthaquinone or β -oximinonaphthol.

From these isomeric di-iminonaphthol hydrochlorides ammonia separates identical bases, but dissociation into base and hydrogen chloride is peculiar to the normal or α -salt; the β -salt, which does not dissociate, decomposes immediately into β -oximinonaphthol and ammonia.

The decomposition of the hydrochlorides in aqueous solution proceeds normally at temperatures up to about 60° , beyond which the primary products of the reaction yield two secondary products: (1) a dark blue colouring matter, which results from the condensation of α -oximinonaphthol and dissolves in alcohol, giving a blue solution with an intense brick-red fluorescence; it dissolves in varying degree in the products of the reaction, and of the product obtained at 94° it forms about 0.5%. (2) 2-Hydroxy- α -naphthaquinone, which is formed by hydration of the amino-group of aminoquinone, $\cdot\text{NH}_2 + \text{H}_2\text{O} = \cdot\text{ONH}_2$. The velocity of this hydration differs for these three quinones, being almost negligible for amino- α -naphthaquinone, only slightly greater for β -oximinonaphthol, and more or less considerable for α -oximinonaphthol. Hence, when the hydration is continued for only ten hours, it may be assumed that the 2-hydroxy- α -naphthaquinone formed is derived entirely from α -oximinonaphthol.

The actual amounts of the three primary products of the reaction are calculated from the equations: (I) amino- α -naphthaquinone = $\alpha + 0.046\alpha + 0.84$; (II) α -oximinonaphthol = $\beta - 0.046\alpha - 4.20 + 0.247$, and (III) β -oximinonaphthol = $\beta' - 0.47\beta'/100 + 4.20$, where α , β , and β' are the experimental quantities of the three products per 100 grams of the hydrochloride.

When crystallised from dilute hydrochloric acid, all the different modifications of the hydrochloride are converted into one and the same form, identical in its decomposition products with that obtained by repeated crystallisation of the crude salt from water. This salt, termed the *A*-salt, is the one mostly employed in the present investigation.

In the decomposition of the hydrochloride (*A*-salt) by acid, the yields of amino- α -naphthaquinone and of α -oximinonaphthol obtained are diminished by repeated crystallisation from either water or acid, and the same is the case with the amount of α -oximinonaphthol converted into hydroxynaphthaquinone and colouring matter; on the other hand, the proportions of β -oximinonaphthol formed gradually increase. By two or three crystallisations from 95% alcohol, the *A*-salt is transformed into another, which has constant properties and is termed the *B*-salt. If the conversion of the *B*-salt into the *A*-salt by crystallisation from *N*/10-hydrochloric acid is determined by absorption of the acid by the salt, the inverse change consists in the gradual removal of the acid from the salt under the influence of the solvent. The *A*-salt must hence contain, not only chemically combined, non-esterifiable acid, but also a certain amount of acid in another form of combination, and capable of esterification by the action of alcohol.

The change produced in the *A*-salt by crystallisation is also effected by prolonged heating or by remaining over sodium hydroxide.

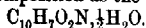
From these results it appears highly probable that the principal

part in the transformations of di-iminonaphthol hydrochlorides is played by traces of free hydrochloric acid fixed by the crystals on their formation in an acid solution, the maximum and minimum (zero) of such fixation being represented by the *A*- and *B*-salts respectively.

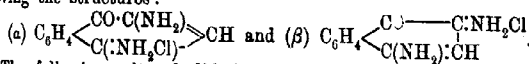
The composition of the *B*-salt having been found to vary with the acidity of the surrounding medium, a *C*-salt, the acidity of which remains constant, was prepared by suitable heating and crystallisation. When this salt is heated with dilute hydrochloric acid solutions of different concentrations, it is found that the transformation of the *B*-salt reaches its limiting value with 0.018 mol. of hydrochloric acid per mol. of *C*-salt, further addition of acid producing no extra increase in the yield of amino- α -naphthaquinone. The amounts of (1) amino- α -naphthaquinone, (2) α -oximinonaphthol, (3) β -oximinonaphthol, and (4) 2-hydroxy- α -naphthaquinone obtained with different concentrations of hydrochloric acid are shown in the form of curves. The second and third curves are approximately straight lines and are therefore in good agreement with the law of mass action. Curve (1), however, rises at first rapidly and then gradually to a limit, its course being closely similar to that of an adsorption curve. It seems, therefore, that when di-iminonaphthol is crystallised from water containing free hydrochloric acid, the latter is adsorbed to some extent on the faces of the crystals. Thus, adsorption in a heterogeneous system is not limited to substances in a colloidal state, but takes place also with crystalloids.

Further experiments show that in a 1% solution of the *B*-salt maintained at 94.5°, two processes occur simultaneously: (1) decomposition of the normal *A*-salt in 0.66% solution, with formation of α - and β -aminonaphthaquinones, and (2) decomposition of the β -salt, not yet isolated, in 0.33% solution, with formation of β -oximinonaphthol.

β -Oximinonaphthol crystallises in shining, flat, reddish-brown needles having the same composition as the α -compound,



The two isomeric di-iminonaphthol hydrochlorides are regarded as having the structures:



The following salts of di-iminonaphthol have been prepared and analysed: the normal *sulphate*, $(\text{C}_{10}\text{H}_7\text{ON}_2)_2 \cdot \text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$; the *acid acetate*, $\text{C}_{10}\text{H}_7\text{ON}_2 \cdot 2\text{C}_2\text{H}_3\text{O}_2$, and the normal *acetate*, $\text{C}_{10}\text{H}_7\text{ON}_2 \cdot \text{C}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$.

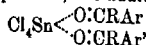
T. H. P.

Lakes. II. PAUL PFEIFFER [and PH. FISCHER, J. KUNTNER, P. MONTI, and Z. PROS] (*Annalen*, 1913, 398, 137—196. Compare A., 1911, i, 899).—The main object of the paper is to show that in hydroxyketones and hydroxyquinones, particularly of the anthraquinone series, the formation of normal salts occurs quite differently from that of internally complex salts.

The author has already shown in connexion with his theory of

halochromy (A., 1911, i, 788) that carbonyl compounds and stannic chloride form additive compounds of the type $\text{Cl}_4\text{Sn} \begin{smallmatrix} \text{O:CRR'} \\ \text{O:CRR'} \end{smallmatrix}$. When the ketone or quinone contains a hydroxyl group in the ortho position to the carbonyl group, a substituted compound is formed which is represented by the formula $\begin{smallmatrix} \text{RC=O} \\ | \\ \text{Ar-O} \end{smallmatrix} \text{SnCl}_2$, and is closely

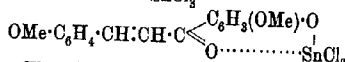
related to the tin lakes (*loc. cit.*). The correctness of this view is supported by the following new facts. Acetophenone, benzophenone, xanthone, and *p*-methoxychalkone form with stannic chloride additive compounds of the first type, whilst their *o*-hydroxy-derivatives yield substituted, internally complex salts of the second type. The formation of the substituted compound is preceded by that of the additive compound because in the cases of *o*-hydroxyacetophenone, resacetophenone, and benzylidenepaeonol, the additive compound,



can be isolated; by loss of hydrogen chloride, it changes to the internally complex salt, $\begin{smallmatrix} \text{RC:O} \\ | \\ \text{Ar-O} \end{smallmatrix} \text{SnCl}_2$. So also, alizarin dimethyl ether and stannic chloride in dry benzene at the ordinary temperature yield $\text{Cl}_4\text{Sn} \dots \text{OC} \begin{smallmatrix} \text{C}_6\text{H}_3 \\ \text{C}_6\text{H}_2(\text{OMe})_2 \end{smallmatrix} \text{CO}$, which is converted by warming into $\text{Cl}_4\text{Sn} \begin{smallmatrix} \text{O:C} \\ | \\ \text{O-C}_6\text{H}_2(\text{OMe}) \end{smallmatrix} \text{CO}$, methyl chloride being evolved.

The theory that the SnCl_2 compounds are internally complex salts containing $\text{Sn} \dots \text{O}$ is supported by the fact that the colours of these substances are in harmony with the generalisations made with respect to the colours of SnCl_4 additive compounds (*loc. cit.*); for example, in the case of resacetophenone derivatives, $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ | \\ \text{O-SnCl}_3 \\ \text{CMe:O} \end{smallmatrix}$ is colour-

less, $\text{CHPh:CH} \cdot \text{C} \begin{smallmatrix} \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{O} \\ | \\ \text{O} \dots \text{SnCl}_3 \end{smallmatrix}$ is orange-yellow, and



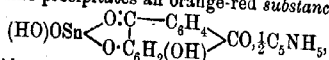
is orange-red. The violet-black colour of the SnCl_2 compound of alizarin (and also of alizarin β -methyl ether), in comparison with the red colour of the SnCl_2 compound of 1-hydroxyanthraquinone, is in agreement with the rule that in halochromatic substances the presence of a hydroxyl or methoxyl group in the meta-position to the carbonyl group causes a deepening of the colour (*loc. cit.*).

Only *o*-hydroxyketones and *o*-hydroxyquinones yield SnCl_2 substituted compounds; the *m*- and *p*-hydroxy-isomerides form SnCl_4 additive compounds of the normal type. *o*-, *m*-, and *p*-Hydroxyacetophenones, benzylidenepaeonol (2-hydroxy-4-methoxyphenyl styryl ketone), phenyl *o*-hydroxystyryl ketone, 1-, 2- and 4-hydroxyxanthones, and 1- and 2-hydroxyanthraquinones have been examined; of these,

hydroxyacetophenone, benzylidenepaeonol, 1-hydroxyxanthone, and hydroxyanthraquinone alone yield SnCl_3 substituted compounds. The fact that resacetophenone, resobenzophenone, 2:4'-dihydroxybenzophenone, euxanthone, and alizarin form mono-substituted SnCl_3 compounds, not disubstituted SnCl_2 compounds, also proves that only the hydroxyl group in the ortho-position to the carbonyl group is concerned in the formation of the internally complex SnCl_3 salt.

The SnCl_3 derivatives of *o*-hydroxyketones and of *o*-hydroxyquinones, being internally complex salts, must be closely related to the tin lakes of these substances, which are typical representatives of internally complex salts (Tschugaeff, A., 1907, i, 17, 392, 830; Werner, A., 1908, 441). On the fibre these lakes do not contain chlorine, and therefore must be derived from the author's compounds simply by replacement of chlorine by oxygen or a hydroxyl group: $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \\ \text{O}-\text{SnCl}_3 \\ \diagdown \\ \text{CR}:\text{O} \end{smallmatrix}$

$\rightarrow \text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \\ \text{O}-\text{SnO(OH)} \\ \diagdown \\ \text{CR}:\text{O} \end{smallmatrix}$. The author shows that the SnCl_3 compounds are converted into tin lakes by hydrolysis. The careful addition of water to the orange solution of the SnCl_3 compound of alizarin in pyridine precipitates an orange-red substance,



which is unstable to acids, stable to aqueous ammonia on the water-bath, and dyes silk and wool, but not cotton, orange-red.

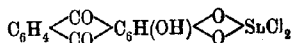
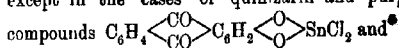
The close relationship between the tin lakes and the author's SnCl_3 compounds is also made evident by the following analogy—only hydroxyketones and quinones containing a hydroxyl group in the ortho-position to the carbonyl group form SnCl_3 compounds—only dyes containing a hydroxyl group in the ortho- or peri-position to the chromophoric group are mordant dyes according to Möhlau and Steimming (*Zeitsch. Farb. Text-chem.*, 1904, 3, 358).

According to the preceding, internally complex SnCl_3 salts of hydroxyanthraquinones are obtained by substitution at the ortho-hydroxyl group. Hence it might be anticipated that this hydroxyl group is also concerned in the formation of the normal salts. Experiment shows that this is not so; 1-hydroxyanthraquinone and quinizarin do not form pyridine salts in hot pyridine, whilst 2-hydroxyanthraquinone, 1:6-dihydroxyanthraquinone, alizarin, 1:7-dihydroxyanthraquinone, and purpurin form pyridine salts, the number of pyridine molecules added being equal to the number of hydroxyl groups in the meta-position to a carbonyl group.

Hence in the formation of normal salts with weak bases just those hydroxyl groups are concerned which do not exhibit any tendency to complex salt formation with tin tetrachloride. Strong bases, such as the hydroxides of the alkali and the alkaline earth metals, react with both *m*- and *o*-hydroxyl groups, but preferably with the former; hydroxyanthraquinone dissolves easily in 1% aqueous sodium carbonate, whilst 1-hydroxyanthraquinone does not. It follows from the preceding that hydroxyl groups in the ortho-

position to the carbonyl group are concerned in complex salt formation, whilst the production of normal salts is due primarily to hydroxyl groups in the meta-position, normal salt formation at an *o*-hydroxyl group being a secondary effect. This is readily explicable. The hydrogen atom of the *o*-hydroxyl group is attached co-ordinatively to the oxygen atom of the carbonyl group and therefore its acidic function is weaker than that of the hydrogen atom of the hydroxyl group in the meta-position. Normal salt formation, therefore, occurs firstly at the *m*-hydroxyl group by the addition, in accordance with the modern view of the phenomenon of neutralisation, of the hydroxide, with the formation of an aquo-salt which then loses water.

The compounds obtained by the action of stannic chloride on hydroxy-acetophenones, hydroxychalcones, hydroxybenzophenones, and hydroxy-xanthenes are described. The production of a SnCl_4 additive compound or of an SnCl_3 substituted compound, and also the colours of the products, are quite in accordance with the rules previously stated except in the cases of quinizarin and purpurin which yield the

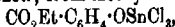


respectively.

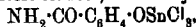
The following *substances* have been prepared by warming the carbonyl compound with stannic chloride, alone or in the presence of dry benzene: $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OSnCl}_3) \cdot \text{COMe}$, m. p. about 235° , almost colourless leaflets containing $\frac{1}{2}\text{C}_6\text{H}_6$, from paeonol;



m. p. 230° , colourless leaflets, from methyl salicylate;



m. p. about 220° , colourless leaflets, from ethyl salicylate;



m. p. about 260° , white crystals containing $\frac{1}{2}\text{C}_6\text{H}_6$, from salicylamide;

$\text{OH} \cdot \text{C}_6\text{H}_3(\text{OSnCl}_3) \cdot \text{COPh}$, m. p. $295\text{--}297^\circ$, yellow crystals containing

$\frac{1}{2}\text{C}_6\text{H}_6$, from resobenzophenone; $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OSnCl}_3) \cdot \text{COPh}$, m. p.

about 262° , yellow crystals, from resobenzophenone methyl ether;

$\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OSnCl}_3$, m. p. $294\text{--}296^\circ$, yellow leaflets, from

2:4'-dihydroxybenzophenone; $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{OSnCl}_3$, m. p.

$282\text{--}284^\circ$, yellow crystals containing $\frac{1}{2}\text{C}_6\text{H}_6$, from 1-hydroxy-

xanthone; $\text{SnCl}_4 \cdot 2\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{OH}$, m. p. 239° , yellowish-brown

powder, from 2-hydroxyxanthone; $\text{SnCl}_4 \cdot \text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{OH}$, m. p.

about 230° , yellow crystals, from 4-hydroxyxanthone (m. p. 242° ,

not 224° as stated in the literature);

$\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OSnCl}_3) \cdot \text{CO} \cdot \text{CH} \cdot \text{CHPh}$,

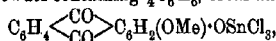
m. p. about 278° , orange-yellow, crystalline powder, from benzylidene-

paeonol; $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OSnCl}_3) \cdot \text{CO} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, m. p. indefinite at

about 250° , orange-red crystals containing $\frac{1}{2}\text{C}_6\text{H}_6$, from *p*-anisylidene-

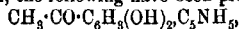
paeonol; $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OSnCl}_3) \cdot \text{CO} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_3 \cdot \text{O}_2 \cdot \text{CH}_3$, decomp. above

200°, orange-red crystals containing $\frac{1}{2}\text{C}_6\text{H}_6$, from piperonylidene-paeonol;
 $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2 \cdot \text{OSnCl}_3$, brownish-red powder containing $\frac{1}{2}\text{C}_6\text{H}_6$,
 from 1-hydroxyanthraquinone; $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2(\text{OH}) \cdot \text{OSnCl}_3$, violet-
 black, crystalline powder containing $\frac{1}{2}\text{C}_6\text{H}_6$, from alizarin;

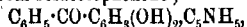


violet-black powder containing $\frac{1}{2}\text{C}_6\text{H}_6$, from alizarin β -methyl ether;
 $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{C}_6\text{H}_3 \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix} \text{SnCl}_2$, red, crystalline powder, from quinizarin;
 $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{C}_6\text{H}(\text{OH}) \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix} \text{SnCl}_2$, almost black, crystalline powder
 containing C_6H_6 , from purpurin; $\text{SnCl}_4 \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2(\text{OMe})_2$,
 brownish, or golden-yellow leaflets, from alizarin dimethyl ether;
 $\text{SnCl}_4 \cdot 2\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2(\text{OMe})_2$, m. p. 242°, brownish-orange leaflets,
 from hystazarin dimethyl ether.

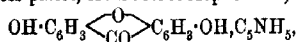
In addition to the normal pyridine salts of the hydroxyanthraquinones
 previously mentioned, the following have been prepared:



colourless crystals, from resacetophenone;



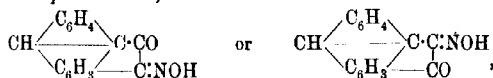
m. p. 58°, colourless plates, from resobenzophenone;



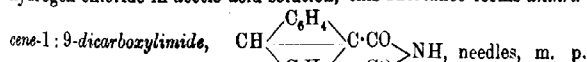
yellow needles, from euxanthone.

C. S.

Some Derivatives of Aceanthrenequinone and 1:9-Anthracene. M. KARDOS (*Ber.*, 1913, 46, 2086—2091).—The action of aceanthrenequinone with an equimolecular proportion of hydroxylamine hydrochloride and a half-molecular proportion of sodium carbonate in the presence of alcohol at water-bath temperature, yields *aceanthrenequinoneoxime*,

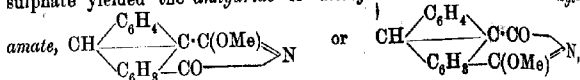


yellow prisms, m. p. 251° (decomp.), which dissolves in sulphuric acid to a brown colour changing to red on warming. When caused to undergo the Beckmann rearrangement, by heating for several hours with hydrogen chloride in acetic acid solution, this substance forms *anthracene-1:9-dicarboxylimide*,



293—294°, which is reducible by alkaline reducing agents to a yellow solution, and dissolves in sulphuric acid to a beautiful red solution which fluoresces slightly; there are obtained simultaneously *anthracene-1:9-dicarboxylic acid*, which readily passes into its *anhydride*, m. p. 289—290° (*methyl ester*, m. p. 149°), and also *anthracene-1:9-dicar-*

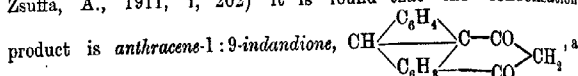
bozylamic acid, which in the free state rapidly passes into the imide; its solutions in alkali exhibit a beautiful sky-blue fluorescence; the sodium and silver salts were analysed. Endeavours to methylate the remaining carboxylic group of the acid amide by means of methyl sulphate yielded the anhydride of methyl anthracene-1:9-carboxyl.



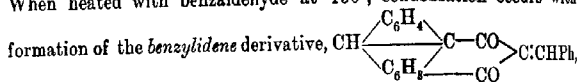
m. p. 170—171°.

Anthracene-1:9-dicarboxylimide is obtainable in theoretical yield by warming aceanthrenequinoneoxime with sulphuric acid for about a half-hour; heating with potassium hydroxide and a little water at 200—230° converts the imide into a green dye, $\text{C}_{18}\text{H}_{12}\text{O}_4\text{N}_2$; this on reduction by hyposulphite yields a red vat which colours cotton reddish-violet, passing on exposure to the air to a beautiful green. Similar dyes can be produced from halogen-substituted aceanthrenequinones.

In an examination of the action of malonyl chloride on anthracene (compare Freund and Fleischer, A., 1910, i, 490; Liebermann and Zsuffa, A., 1911, i, 202) it is found that the condensation



red powder, m. p. 280° (decomp.) with previous blackening, which in sulphuric acid gives a carmine-red solution with a strong fluorescence; sodium salt, red leaflets. On oxidation with alkaline potassium permanganate solution, it produces anthraquinone-1-carboxylic acid. When heated with benzaldehyde at 130°, condensation occurs with



a brownish-red powder, decomp. at 290°, which gives a reddish-violet solution in sulphuric acid.

D. F. T.

Influence of Constitution on the Rotatory Power of Optically Active Substances. V. Keto-enolic Transformations of Derivatives of Menthyl Acetoacetates. HANS RUPP and EDUARD LENZINGER (*Annalen*, 1913, 398, 372—378).—*l*-Menthyl *d*-phenylacetoacetate exists in the solid state as the ketonic modification. In benzene it is initially dextrorotatory, but in course of time becomes levorotatory as the change to the enolic modification proceeds and the *l*-menthyl group becomes the only source of optical activity. It has previously been shown that the rate of transformation is very variable, and been suggested that this variation is caused by the presence of catalysts such as the alkali in the glass vessel. This hypothesis has now been proved. A 9.958% solution, D_D^{20} 0.8891, of *l*-menthyl *d*-phenylacetoacetate in benzene containing a trace of piperidine had $[\alpha]_D^{25} + 26.09^\circ$ initially and a final constant value, $[\alpha]_D^{25} - 67.20^\circ$ after ten hours. A similar solution ($c = 10.02$, $D = 0.8895$) containing a drop of piperidine

had initially $[\alpha]_D^{20} + 26.23^\circ$, and a final constant value, -67.09° , after eight minutes. Within certain limits, the velocity of the keto-enolic change is a function of the concentration of the catalyst.

l-Menthyl *d*-benzoylphenylacetate exhibits a constant rotation in benzene; also, its alcoholic solution does not develop a coloration with ferric chloride. Hence the stability of the ketonic modification is greatly increased when the methyl group in menthyl phenylacetate is replaced by a phenyl group. However, again the presence of a trace of piperidine increases the velocity of the change from the ketonic to the enolic modification because a solution ($c = 9.98$, $D_4^{20} 0.8924$) of *l*-menthyl *d*-benzoylphenylacetate in benzene containing a trace of piperidine has $[\alpha]_D^{20} + 20.76^\circ$ initially and -62.83° after eighteen hours.
C. S.

Cardol. LEOPOLD SPIEGEL and M. CORELL (*Ber. Deut. pharm. Ges.*, 1913, 23, 356—378. Compare Spiegel and Dobrin, A., 1896, i, 653).—Cardol can be distilled in superheated steam or under reduced pressure. In the latter case the principal fraction has b. p. $190^\circ/3$ mm., but is of variable composition, as shown by the analysis of two specimens. It is named *apocardol*, and its reactions with bromine, ozone, permanganate, nitric acid, and on distillation with zinc dust are described. In most cases these do not lead to well-defined products, but the zinc dust distillation yielded ethylene, propylene, 1:3-butadiene, and a substance, $C_{12}H_{12}O$, m. p. 10° , b. p. $98-100^\circ/14$ mm.

In addition to *apocardol* a fraction, b. p. $200-220^\circ/2-5$ mm., is obtained.
T. A. H.

Constituents of Ethereal Oils. Eudesmol and its Derivatives. Globulol. FRIEDRICH W. SEMMLER and ERNST TOBIAS (*Ber.*, 1913, 46, 2026—2032).—The authors have carried out a series of experiments on the sesquiterpene alcohols, eudesmol, which is widely distributed in eucalyptus oils, and globulol, which occurs in the ethereal oil from *Eucalyptus Globulus*. The former has been investigated by Baker and Smith, who consider it to be an oxide having the formula $C_{10}H_{16}O$, and describe a dinitro-derivative, $C_{10}H_{14}(NO_2)_2O$, and a dibromide, $C_{10}H_{16}OBr_2$. The authors, however, are led to the conclusion that it is a bicyclic sesquiterpene alcohol, $C_{15}H_{26}O$, containing one double bond.

Eudesmol has b. p. $156^\circ/10$ mm., $D_4^{20} 0.9884$, $n_D^{20} 1.516$, m. p. 78° (Baker and Smith give m. p. $79-80^\circ$), $[\alpha]_D^{20} + 31.21'$ in chloroform solution. When boiled with acetic anhydride and sodium acetate, it yields *eudesmol acetate*, $CH_3 \cdot CO_2 \cdot C_{15}H_{25}$, b. p. $165-170^\circ/11$ mm., $D_4^{20} 0.9933$, $n_D^{20} 1.49204$, $[\alpha]_D^{20} + 31^\circ$.

Dihydroeudesmol, $C_{15}H_{28}O$, b. p. $155-160^\circ/12.5$ mm., m. p. 82° , is obtained when an ethereal solution of eudesmol is reduced by hydrogen in the presence of platinum. When treated with sodium acetate and acetic anhydride, it yields the corresponding *acetate*, b. p. $158-164^\circ/10$ mm., $D_4^{20} 0.9776$, $n_D^{20} 1.4788$, $[\alpha]_D^{20} + 13^\circ$, from which *dihydroeudesmol* is recovered unchanged after saponification with

alcoholic potassium hydroxide. When boiled with absolute formic acid, dihydroeudesmol yields *dihydroeudesmene*, $C_{15}H_{26}$, b. p. 126—130°/10 mm., D^{20}_D 0.9087, n^{20}_D 1.48762, $[\alpha]^{20}_D$ -7°.

Eudesmene, $C_{15}H_{24}$, obtained when eudesmol is heated with 90% formic acid, has b. p. 129—132°/10 mm., D^{20}_D 0.9204, n^{20}_D 1.50738, $[\alpha]^{20}_D$ +49°, and is thus apparently a member of the sesquiterpenes derived from hydrogenated naphthalenes. It yields a characteristic *dihydrochloride* and *dihydrobromide*. The former, m. p. 79—80°, is obtained either by treatment of eudesmol with a saturated solution of hydrogen chloride in glacial acetic acid or by passing hydrogen chloride into eudesmene dissolved in the same solvent. The hydrocarbon is regenerated when the dihydrochloride is boiled with alcoholic potassium hydroxide. The dihydrobromide, m. p. 104—105°, can be prepared by precisely similar methods, and also gives eudesmene when acted on by alcoholic potassium hydroxide.

When treated with zinc dust, eudesmol gives a small quantity of the hydrocarbon, $C_{15}H_{26}$, but is mainly converted into eudesmene. The latter substance is also obtained when phosphorus pentachloride reacts with eudesmol. Oxidation with ozone or potassium permanganate did not lead to definite results.

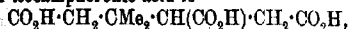
Globulol, $C_{15}H_{26}O$ (compare A., 1904, i, 604), has b. p. 283°/755 mm. It differs physically from eudesmol, but, possibly, similar relationships exists between the two alcohols as between borneol and isoborneol; otherwise they are chemically different. When treated with dehydrating agents, globulol yields a *l-sesquiterpene*, $C_{15}H_{24}$, b. p. 102—103°/6 mm., 247—248°/748 mm., $[\alpha]^{20}_D$ -55°48', n^{20}_D 1.49287, D^{18}_D 0.8956, and a *d-sesquiterpene*, $C_{15}H_{24}$, b. p. 265.5—266°/750 mm., α_D +58°40', n^{20}_D 1.50602, D^{18}_D 0.9236. The latter is possibly identical with eudesmene. H. W.

Determination of Constitutions in the Camphene Group.
V. OSSIAN ASCHAN (*Annalen*, 1913, 398, 209—313).—Since Auwers has recently upheld, on refractometric evidence, Wagner's formula for camphene, the author has examined two carefully purified specimens of the hydrocarbon. These have been obtained from American and Grecian turpentine respectively, through the pinene hydrochlorides. Each has been twice recrystallised from methyl alcohol (whereby the m. p. is constant), and finally distilled over sodium in a vacuum. The camphene from American turpentine has b. p. 158—158.5°, m. p. 43—43.5°, D^{20}_D 0.8486, n^{20}_D 1.46048, and $[\alpha]^{18}_D$ +17.95° in benzene. The camphene from Grecian turpentine has b. p. 157.2—157.9°/742 mm., m. p. 46—47°, D^{20}_D 0.8446, n^{20}_D 1.45641, and $[\alpha]^{20}_D$ +74.55° in benzene. The molecular refractions, 43.98 and 43.85 respectively, are in close agreement with the value, 43.91, calculated for the semicyclic formula.

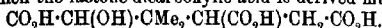
The formula $\begin{array}{c} CH_2 \cdot CH_2 \\ \diagup \quad \diagdown \\ CO \quad O \end{array} > C(CO_2H) \cdot CMe_2 \cdot CO_2H$ previously assigned

by the author (A., 1910, i, 710) to the lactone-dicarboxylic acid, m. p. 256°, obtained from dehydrocamphenic acid, is now proved to be incorrect. The lactone-dicarboxylic acid is reduced to *isocamphoronic*

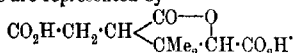
acid by hydriodic acid, b. p. 127—128°, at 170—180°. Since the constitution of *isocamphoronic* acid is



and the lactone-dicarboxylic acid yields formic, succinic, and *isobutyric* acids by fusion with potassium hydroxide, it follows that the hydroxy-acid from which the lactone-dicarboxylic acid is derived must be •



By boiling with hydriodic acid, by heating with 40% hydrogen bromide in glacial acetic acid, or with concentrated sulphuric acid at 100°, or with hydrochloric acid at 170—180°, the lactone-dicarboxylic acid is changed into a stereoisomeric *lactone-dicarboxylic acid*, $\text{C}_9\text{H}_{12}\text{O}_6$, m. p. 185—186°, large prisms. Such stereoisomerism is possible only when at least two side-chains are present attached to different carbon atoms of the lactone ring. Hence the constitutions of the two lactone-dicarboxylic acids are represented by



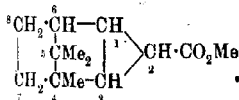
On account of its sparing solubility, the isomeride, m. p. 256°, is regarded as having the *trans*-configuration.

The author is of opinion that Wagner's formula correctly represents the constitution of camphene. If this is the case, it follows from the preceding work that a transformation must have occurred in the carbon skeleton during the oxidation of camphene by alkaline potassium permanganate.

C. S.

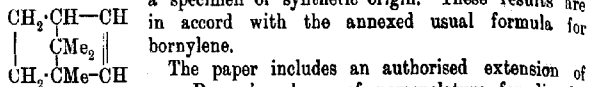
Bornylene and Ethyl Diazoacetate (with a Nomenclature for Tricyclic Carbon Ring Systems). EDUARD BUCHNER and WILHELM WEIGAND (*Ber.*, 1913, 46, 2108—2117).—The constitution of camphene has recently been demonstrated in a purely chemical manner by the action of ethyl diazoacetate, and the same method is now applied to bornylene (this vol., i, 376). The results indicate that this reagent is of especial value for distinguishing between hemicyclic and endocyclic ethylenic linkings in terpene molecules.

The bornylene applied in this investigation, obtained from borneol through the corresponding methyl xanthate compound, was possibly not quite pure, as its optical activity was somewhat lower than that recorded in the literature; the impurities, however, could not be of such a nature as to affect the trustworthiness of the reaction with ethyl diazoacetate. A solution of ethyl diazoacetate in a little borneol was gradually introduced into a mixture of borneol with a little copper powder at 150°; the reaction is more sluggish than with camphene, but fractional distillation of the product separated *methyl 4:5:5-trimethyltricyclo-[0,1,3^{4,6},2]octane-2-carboxylate* (annexed formula), a colourless oil, b. p. 136—137°/22 mm., D_4^{20} 1.0283, n_D^{20} 1.48337, $[\alpha]_D^{25}$ -8.72°.



By hydrolysis with alcoholic potassium hydroxide, the corresponding acid is obtained, leaflets, m. p. 137°; calcium, barium, lead, and silver salts, colourless, insoluble substances; amide, needles, m. p. 174°

When the acid is heated with an acid solution of potassium permanganate, oxidation slowly occurs with formation of an oily substance, *trans*-cyclopropane-1:2:3-tricarboxylic acid, which very gradually crystallised. The identity of this acid was confirmed by the preparation of the silver and calcium salts and of the methyl ester, the m. p., 56—57°, of which was unaffected by admixture with a specimen of synthetic origin. These results are in accord with the annexed usual formula for



The paper includes an authorised extension of von Baeyer's scheme of nomenclature for bicyclic systems to tricyclic ones. Each tricyclic system contains two tertiary or quaternary carbon atoms in the ring, which are linked by bridges of carbon chains; these bridges, of which there are four in each tricyclic system, are represented by numbers which represent the number of atoms in each; the grouping of these 4 numbers constitutes the "characteristic"; if these bridges do not extend between the same carbon atoms in each case, the numbers representing the carbon atoms which act as origin and extremity of the bridge must be appended to the corresponding number in the characteristic. The application of this scheme can be seen in the above description of the condensation product of bornylene and ethyl diazoacetate.

D. F. T.

The Synthesis of the Glucosides of the Terpene Alcohols by means of Emulsin. JUHO HÄMÄLÄINEN (*Biochem. Zeitsch.*, 1913, 52, 409—411).—The author has shown (this vol., i, 497, 639) that certain glucosides of the terpene alcohols are readily hydrolysed by emulsin. It seemed therefore possible that synthesis could be effected by the same agency. He has succeeded in obtaining in small quantities synthetically the following glucosides, by allowing the alcoholic solutions of dextrose and the alcohol to react in the presence of emulsin in ethyl alcoholic solutions: *l*-fenchyl-*d*-glucoside, *r*-isoborneol-*d*-glucoside, and *l*-borneol-*d*-glucoside. The formation of these glucosides can explain the action of emulsin in producing glycuronates of terpene-alcohols when injected into animals. A synthetic action of the ferment seems more probable than the formation of an anti-substance, as suggested by various investigators.

S. B. S.

Synthesis of β -Geranylglucoside by means of Emulsin; Its Presence in Plants. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1913, 157, 72—74).— β -Geranylglucoside is obtained by the action of emulsin on a suspension of dextrose in geraniol saturated with water, or, better, by its action on a solution of the alcohol and sugar in acetone and water. It was separated by the usual method (compare this vol., i, 663), and obtained as a colourless liquid, $[\alpha]_D - 25^\circ 49'$, not reducing Fehling's solution, precipitated by basic lead acetate, and rapidly hydrolysed in aqueous solution by emulsin. A glucoside similarly hydrolysed by emulsin to dextrose and geraniol and precipitated by basic lead acetate can be extracted by alcohol from *Pelargonium odoratissimum*.

W. G.

Cerebronic Acid. III. Its Bearing on the Constitution of Lignoceric Acid. PHCEBUS A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1913, **15**, 193—195).—Cerebronic acid yields a normal acid of 24 carbon atoms which is identical with lignoceric acid. W. D. H.

Azafrin. II. CARL LIEBEGMANN and W. SCHILLER (*Ber.*, 1913, **46**, 1973—1986. Compare A., 1911, i, 391).—Although azafrin and bixin (Hasselt, A., 1911, i, 550) both give blue solutions in concentrated sulphuric acid, they are not identical. This is now shown by the fact that azafrin and methylazafrin give very characteristic colour reactions with a large number of other strong mineral or organic acids, with which bixin gives, at most, only transient and poor effects. One, two, or three molecules of an acid may enter into combination, but the compounds are not simple salts, since azafrin cannot be regenerated from them. Oxidation, reduction, substitution, hydroxyl and keto reactions have either failed or led to still more complicated substances, but, from the analysis of the above compounds, it seems certain that azafrin has the formula $C_{31}H_{42}O_5$.

It is advisable not to prolong the extraction of azafranillo roots and stems, since benzene dissolves a small amount of a resin which hinders the crystallisation of the desired azafrin. The latter is purified by precipitation from alkaline solution, has m. p. 208° , and yields *methyl-azafrin*, $C_{32}H_{44}O_5$, in sparkling, reddish-yellow leaflets or needles, m. p. 191° , when treated with methyl sulphate. The following compounds with acids have been isolated: $B_2 \cdot 2H_2SO_4$, $B_3 \cdot 3HI$, $B_2 \cdot 2HBr$, $B_3 \cdot 3HCl$, $B_3 \cdot HClO_4$, and $B_3 \cdot 3CCl_3 \cdot CO_2H$, where B = azafrin or methylazafrin. They are blue or violet in colour, and dissolve in alkalis with never more than partial loss of acid. Phosphoryl chloride, metaphosphoric acid, and nitric acid also give coloured solutions, but especially characteristic is the reaction with hot anhydrous formic acid, which gives a deep violet solution which may be diluted with water to a stable permanganate-coloured liquid. Glacial acetic acid is a useful indifferent solvent for azafrin, but after boiling the solution for a long time, water precipitates an entirely different substance.

Reduction of azafrin and methylazafrin with zinc dust and acids yields white, amorphous products, $C_{31}H_{46}O_4$ and $C_{32}H_{48}O_4$ respectively, whilst hydriodic acid and red phosphorus give rise to compounds which contain phosphorus. Ammonium persulphate yields a white, flocculent acid. J. C. W.

The Hydrogenation of Pyromucic Acid. HEINRICH WIENHAUS and HERMANN SORGE (*Ber.*, 1913, **46**, 1927—1931).—Only in a few cases in the furan group have reductions been effected by hydrogen. The author, in this preliminary announcement, describes tetrahydro-pyromucic acid obtained by the reduction of pyromucic acid with hydrogen and colloidal palladium.

Tetrahydropyromucic acid, $\begin{array}{c} CH_2 \cdot CH_2 \\ | \quad \quad | \\ CH_2 - O \end{array} > CH \cdot CO_2H$, was prepared by adding to the aqueous solution of pyromucic acid a little palladium

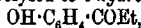
chloride solution and gum arabic, and shaking with hydrogen. The acid was purified by distillation, b. p. 131°/14 mm., and then crystallises in rhombohedra, m. p. 21°. It is much more stable than pyromucic acid towards potassium permanganate. The sodium salt crystallises in thin tablets; the potassium, ammonium, barium, and silver salts are all crystalline. When treated with phosphorus trichloride, the free acid is converted into the chloride, which reacts with strong ammonia solution, producing the amide, leaflets, m. p. 80°, b. p. 135–140°/20 mm. The same amide is formed when the ammonium salt is heated at 200° under pressure.

D. F. T.

A New Chromone Synthesis. ERNST PETSCHER and HUGO SIMONIS (*Ber.*, 1913, 46, 2014–2020).—When phenols are condensed with β -ketonic acid esters in presence of sulphuric acid, the products are coumarin derivatives (1:2-benzopyrones), but when phosphoric oxide is used, chromones (1:4-benzopyrones) are obtained. Ethyl acetoacetate itself has not yet led to definite products, but this method is being extended, particularly with a view to the synthesis of flavone from ethyl benzoylacetate and phenol.

For the preparation of 2:3-dimethylchromone, $C_6H_4 \begin{smallmatrix} \diagup O-CMe \\ | \\ CO-CMe \end{smallmatrix}$ the dark mass obtained by mixing a solution of dry phenol in ethyl methylacetoacetate with phosphoric oxide is diluted with water, treated with half the quantity of sodium hydroxide required to neutralise the acid, saturated with salt, and extracted with ether. The extract is washed with alkali, dried, and evaporated. The yield is 25%. The compound forms large, transparent, yellow, monoclinic crystals [$\alpha:b:c = 1.5201:1:1.5681$, $\beta = 73^\circ 19' 5''$], m. p. 97°. One litre of water dissolves 0.5 gram at 0°, 1.5 grams at 15°, and 4.5 grams at 100°, and the substance is volatile in steam. It forms a dibromide, $C_{11}H_{10}O_2Br_2$, in unstable, orange-yellow needles, m. p. 130°, and an oxime, $C_{11}H_{10}O:N\cdot OH$, by the direct action of hydroxylamine, in colourless, silky needles, m. p. 158.5°. The isomeric 3:4-dimethylcoumarin oxime, prepared from 3:4-dimethylthiocoumarin, m. p. 142°, has m. p. 222°. The oxime of the dimethylchromone yields a dibromide, m. p. 180–184°, which readily parts with one molecule of hydrogen bromide to form 2-bromo-4-nitroso-2:3-dimethylcoumaran, $C_6H_4 \begin{smallmatrix} \diagup C(NO):CMe \\ | \\ O-CBrMe \end{smallmatrix}$, in colourless needles, m. p. 205°.

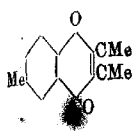
2:3-Dimethylchromone is easily oxidised by permanganate or hydrolysed by 3% sodium hydroxide, yielding salicylic acid. When heated with sodium ethoxide (compare Heywang and Kostanecki, *A.*, 1902, i, 816) it is hydrolysed to *o*-hydroxypropiophenone,



which forms a colourless, mobile, unpleasant smelling oil, b. p. 150°/80 mm. It is sparingly soluble in water, and the solution gives an intense reddish-violet coloration with ferric chloride. The hydrochloride of dimethylchromone, $C_6H_4 \begin{smallmatrix} \diagup O(HCl):CMe \\ | \\ CO-CMe \end{smallmatrix}$, is a white, crystal-

fine substance, m. p. 88–92°. On nitration with fuming acid in cold concentrated sulphuric acid, 6-nitro-2:3-dimethylchromone, $\text{NO}_2\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{O}-\text{CMe} \\ | \\ \text{CO}\cdot\text{CMe} \end{smallmatrix}$ is obtained in colourless prisms, m. p. 163°,

which dissolve in potassium hydroxide with intense yellow colour. The isomeric 6-nitro-3:4-dimethylcoumarin, $\text{C}_{11}\text{H}_9\text{O}_4\text{N}$, from 3:4-dimethylcoumarin has m. p. 172°. Both compounds yield 5-nitrosalicylic acid on oxidation. 7(1)-Chloro-6-amino-2:3-dimethylchromone, $\text{C}_{11}\text{H}_{10}\text{O}_2\text{NCl}$, is obtained when the nitro-compound is reduced by means of tin and hydrochloric acid. It has m. p. 245°, absorbs bromine, and yields a dark red chlorohydroxydimethylchromone.



p-Cresol and ethyl methylacetacetate condense to form 2:3:6-trimethylchromone (annexed formula) in long, colourless, sparkling needles, m. p. 107°, which yield 5-methylsalicylic acid on hydrolysis with dilute alkali. Similarly, *m*-cresol yields 2:3:7(or 5)-trimethylchromone, in clusters of colourless needles, m. p. 96°. The oxidation to a methylsalicylic acid has met with difficulties.

J. C. W.

A Simple Process for the Preparation of Flavones. Synthesis of Thioflavone. SIEGFRIED RUHEMANN (*Ber.*, 1913, 46, 2188–2197).—The author has succeeded in condensing β -oxyaryl-cinnamic acids to flavones by heating their chlorides with aluminium chloride. Flavones which are substituted in position 8, ortho to the pyrone oxygen, do not show the fluorescence in concentrated sulphuric acid which is characteristic of these compounds in general. In the case of the hydroxyflavones, the removal of the hydroxyl group from the pyrone oxygen is accompanied by a constant depression of the melting point.

The condensation is carried out by adding phosphorus pentachloride to a suspension of the acid in dry benzene and warming until solution takes place, when aluminium chloride is introduced into the product. In this way β -phenoxycinnamic acid (*T.*, 1900, 77, 986) gives an almost theoretical yield of flavone; β -*o*-tolylloxycinnamic acid (*loc. cit.*,

988) forms 8-methylflavone, $\text{C}_{15}\text{H}_{11}\text{O}_2\begin{smallmatrix} \text{CO}\cdot\text{CH} \\ | \\ \text{O}-\text{CPh} \end{smallmatrix}$, in colourless needles,

m. p. 170°, which are gradually decomposed by boiling concentrated potassium hydroxide into acetophenone; β -*m*-tolylloxycinnamic acid (*loc. cit.*, 1120) yields a mixture of 5- and 7-methylflavones; β -*p*-tolylloxycinnamic acid (*loc. cit.*, 989) gives 6-methylflavone, in colourless needles, m. p. 122–123°, and β -thymoxycinnamic acid (*T.*, 1901, 79, 918) forms 5-methyl-8-isopropylflavone, $\text{C}_{19}\text{H}_{15}\text{O}_2$, which crystallises in colourless needles, m. p. 143–144°. For the preparation of the isomeride of the latter, ethyl phenylpropionate was added to a solution of sodium in excess of carvacrol, the resulting yellow, viscous ethyl β -carvacroxycinnamate, $\text{C}_{18}\text{H}_{15}\text{MePr}\cdot\text{O}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, b. p. 225°/12 mm., was hydrolysed to β -carvacroxycinnamic acid, $\text{C}_{16}\text{H}_{13}\text{O}_2$, which formed well-defined, rhombic crystals from light petroleum, and lost carbon dioxide on heating above 103°, and this acid was treated as

above. 8-Methyl-5-isopropylflavone forms colourless prisms, m. p. 149—150°.

Similarly, β -o-methoxyphenoxy-cinnamic acid (T., 1900, 77, 1181) was converted into 8-methoxyflavone, $C_{16}H_{12}O_2$, which crystallised in colourless, silky needles, m. p. 199—200°, and formed 8-hydroxyflavone, $C_{15}H_{10}O_2$, in colourless needles, m. p. 249—250°, by hydrolysis with concentrated hydriodic acid in a sealed tube. Finally, β -phenylthiolcinnamic acid (*ibid.*) was condensed in the same way to thioflavone,

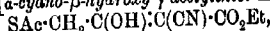
$C_6H_5 \cdot \begin{array}{c} \text{CO} \cdot \text{CH} \\ | \\ \text{S} - \text{CPh} \end{array}$, which forms white needles, m. p. 129—130°, and

dissolves in warm, concentrated hydrochloric acid. The sulphonium salt and the platinichloride are, however, decomposed by water.

J. C. W.

Thiotetronic Acid and Derivatives. EICH BERRY (Ber., 1913, 46, 2103—2107. Compare A., 1910, i, 434, 579).—The results of Anschütz and Bertram (A., 1903, i, 271) suggest that the hitherto unknown thiotetronic acid might be obtained through the interaction of ethyl sodiomalonate and acetylthiolacetyl chloride.

Acetylthiolacetic acid, $\text{SAc} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, is obtained by mixing thioglycolic acid and acetyl chloride, when a vigorous reaction ensues; the acid, b. p. 158—159°/17 mm., which can also be obtained by the interaction of thioacetic acid and chloroacetic acid in alkaline solution, gives a deep blue colour with ferric chloride solution, and is converted by phosphorus pentachloride into acetylthiolacetyl chloride, a pungent liquid, b. p. 93—95°/20 mm. The chloride cooled in ethereal solution reacts with ethyl sodioacetoacetate, yielding ethyl acetylthiolacetylcyanacetate [α -cyano- β -hydroxy- γ -acetylthiol- Δ^4 -butanoate],



colourless needles, m. p. 70—71°, which indicates its enolic character by a red coloration with ferric chloride and by its acidity. Under similar conditions with ethyl sodioacetoacetate, the sodium derivative of ethyl acetylthiolacetylacetoacetate is obtained; the free ester is a heavy, yellow oil which passes very readily with elimination of alcohol

into α -acetylthiotetronic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{OH}) \\ | \\ \text{S} - \text{CO} \end{array} \rightleftharpoons \text{CAc}$, an acidic substance,

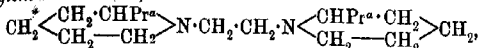
needles, m. p. 86—88°; phenylhydrazones, yellow needles, m. p. 173—174°, of feeble acid properties. In an analogous manner the interaction of acetylthiolacetyl chloride with ethyl sodiomalonate yields oily ethyl acetylthiolacetylmalonate, which on dissolving in sodium hydroxide solution and reprecipitation by acid eliminates a molecule of alcohol with formation of ethyl thiotetron- α -carboxylate, $\begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{OH}) \\ | \\ \text{C} - \text{CO} \end{array} \rightleftharpoons \text{C} \cdot \text{CO}_2\text{Et}$, needles, m. p. 122—123°; this reacts acid

and gives a blood-red coloration with ferric chloride. On boiling with water for an hour, the ester is converted into thiotetronic acid, $\begin{array}{c} \text{S} - \text{CH}_2 \\ | \\ \text{CO} \cdot \text{CH} \end{array} \rightleftharpoons \text{C} \cdot \text{OH}$, colourless needles, m. p. 115—117°, which behaves as a monobasic acid and gives a deep red coloration with ferric chloride;

the silver salt was prepared. With sodium nitrite, its aqueous solution produces a deep violet coloration. • D. F. T.

Isomerism with Diacid Quaternary Ammonium Bases of the Coniine Group. Asymmetric Nitrogen 46. EDGAR WEDEKIND and F. NEY (*Ber.*, 1913, 46, 1895—1899. Compare Wedekind, A., 1912, i, 509, 948).—Although many investigations have been made, in only one case (E. and O. Wedekind, A., 1910, i, 834) have the two isomeric forms of a diquaternary ammonium salt, in which the nitrogen atoms are asymmetric, been isolated. Endeavours have now been made to effect this isolation of the isomerides by using compounds containing an active asymmetric carbon atom. The addition of menthyl indacetate to ditertiary bases is not satisfactory. It was found, however, that the aim could be achieved by the application of diacid bases derived from coniine.

Ethylene-bis-d-coniine,



b. p. 200—203°/19 mm., $[\alpha]_D + 81.09^\circ$, obtained by warming together for three hours a mixture of ethylene bromide with a quadrimolecular proportion of *d*-coniine, reacts with benzyl bromide, producing a mixture of diquaternary ammonium salts with an amine-ammonium salt, but the solubility differences in the products are too small to permit separation. With benzyl iodide the chief product, when the reaction occurs unassisted, is the amine-ammonium salt, decomp. at 178°, but if excess of warm molten benzyl iodide is introduced into the warm ditertiary base the product consists mainly of two diquaternary ammonium salts which can be separated by extraction with a mixture of alcohol and acetone; the more soluble and more abundant isomeride (termed α), prisms, decomp. at 130—131°, has $[\alpha]_D + 40.42^\circ$, whilst the β -isomeride, cubical crystals, decomp. at 214°, has $[\alpha]_D + 15.42^\circ$, the solutions in both cases being observed in methyl alcoholic solution.

From theoretical reasons, three isomerides might be expected, represented by the schemes (N+, C+) . . . (N+, C+), (N-, C+) . . . (N-, C+), and (N+, C+) . . . (N-, C+). The α - and β -forms isolated are believed to be represented by the first two structures, the isomeride of the third configuration being too unstable to exist under the conditions of the experiment and so passing into the first form. This view is confirmed by the fact that the isomeride of higher rotation, and therefore of the first configuration, preponderates in the reaction product.

Trimethylene bis-d-coniine, obtained in an analogous manner from coniine and trimethylene bromide, has b. p. 200—201°/17 mm.; unfortunately, its diquaternary salts with benzyl bromide, benzyl iodide, and methyl iodide are amorphous, whilst with allyl iodide the product, which is at first amorphous, on keeping under ether becomes partly crystalline, but very easily undergoes decomposition. That the last substance is the expected *trimethylenebisallylconiinium iodide* was proved by analysis of the corresponding *platinichloride*. D. F. T.

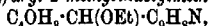
The Behaviour of 2-Methylindole towards Aldehydes and Formic Acid. MAX SCHOLTZ (*Ber.*, 1913, 46, 2138—2146).—The

interaction of 2-methylindole with aldehydes in alkaline media is strikingly different from its behaviour in acid or neutral solution (Fischer, A., 1887, 265; Freund and Lebach, A., 1905, i, 663).

If equimolecular quantities of 2-methylindole and benzaldehyde are treated with sodium hydroxide solution, a reaction occurs in which the solvent is implicated, for the product is *ethoxyphenyl-2-methylindolylmethane*, $\text{OEt} \cdot \text{CHPh} \cdot \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CMe} \end{smallmatrix} \text{NH}$, colourless leaflets, m. p. 123°.

A similar reaction with *p*-tolualdehyde in place of benzaldehyde yields *ethoxy-p-tolyl-2-methylindolylmethane*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH}(\text{OEt}) \cdot \text{C}_6\text{H}_3\text{N}$, colourless prisms, m. p. 101°. If methyl alcohol is applied as solvent instead of ethyl, the product is *methoxy-p-tolyl-2-methylindolylmethane*, $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH}(\text{OMe}) \cdot \text{C}_6\text{H}_3\text{N}$, colourless prisms, m. p. 153°.

Furfuraldehyde, 2-methylindole, and ethyl alcohol under similar conditions yield *ethoxyfuryl-2-methylindolylmethane*,



colourless needles, m. p. 158°. With methyl alcohol as solvent, *methoxyfuryl-2-methylindolylmethane*, $\text{C}_4\text{OH}_3 \cdot \text{CH}(\text{OMe}) \cdot \text{C}_6\text{H}_3\text{N}$, grey prisms, m. p. 108°, is obtained.

The product from anisaldehyde, 2-methylindole, and ethyl alcohol is *ethoxy-p-anisyl-2-methylindolylmethane*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OEt}) \cdot \text{C}_6\text{H}_3\text{N}$, colourless tablets, m. p. 133°; with methyl alcohol the product is *methoxy-p-anisyl-2-methylindolylmethane*, colourless leaflets, m. p. 151°.

o-Chlorobenzaldehyde, 2-methylindole, and ethyl alcohol yield *ethoxy-o-chlorophenyl-2-methylindolylmethane*, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH}(\text{OEt}) \cdot \text{C}_6\text{H}_3\text{N}$, tablets, m. p. 122°; methyl alcohol gives *methoxy-o-chlorophenyl-2-methylindolylmethane*, needles, m. p. 91°.

m-Nitrobenzaldehyde, 2-methylindole, and ethyl alcohol produce *ethoxy-m-nitrophenyl-2-methylindolylmethane*,



yellow leaflets, m. p. 130°; methyl alcohol gives *methoxy-m-nitrophenyl-2-methylindolylmethane*, yellow, rhombic prisms, m. p. 155°.

Nearly all the above products have a tendency to redden if kept in a moist condition.

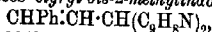
The behaviour of *o*-nitrobenzaldehyde is curiously abnormal, for, whether methyl or ethyl alcohol is used as solvent, and sodium hydroxide or piperidine as alkali, the one product is *o-nitrophenyl-2-methylindolylcarbinol*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{C}_6\text{H}_3\text{N}$, orange-red leaflets, m. p. 138°.

Salicylaldehyde also failed to react in the above general manner with methylindole and alcohol, for under the usual conditions the sodium salt of salicylaldehyde is deposited, whilst if water is added to retain this, *o*-hydroxyphenylidi-2-methylindolylmethane (Freund and Lebach, *loc. cit.*) separates. If, however, the mixture of salicylaldehyde and methylindole in alcohol is made alkaline by piperidine in place of sodium hydroxide, the piperidine nucleus enters into the reaction product, which is *piperidino-o-hydroxyphenyl-2-indolylmethane*, $\text{C}_6\text{H}_4\text{N} \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{OH}) \cdot \text{C}_6\text{H}_3\text{N}$, colourless prisms, m. p. 201°. *p*-Homosalicylaldehyde with piperidine and methylindole in alcoholic solution behaves similarly to salicylaldehyde, producing *piperidine*

o-hydroxy-*m*-tolyl-2-methylindolylmethane,

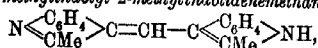
$\text{OH} \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{CH}(\text{C}_6\text{H}_5\text{N}) \cdot \text{C}_6\text{H}_4\text{N}$,
colourless needles, m. p. 132°. These two piperidino-compounds were the only ones obtainable in a crystalline condition, the products from other aldehydes being oily.

That the 3-carbon atom of the pyrrole nucleus is not entirely deprived of its activity in alkaline media is evidenced by the occasional occurrence of traces of di-indolyl derivatives in the reaction product; indeed, with *p*-hydroxybenzaldehyde and cinnamaldehyde the products are entirely of this type. The former aldehyde with piperidine and 2-methylindole in alcoholic solution gives rise to *p*-hydroxyphenyl-bis-2-methylindolylmethane, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_6\text{H}_5\text{N})_2$, a crystalline powder, m. p. 237°; in a similar manner, by condensation of one molecule of aldehyde with two molecules of 2-methylindole, cinnamaldehyde produces *styryl-bis-2-methylindolylmethane*,



yellow needles, m. p. 226°.

A solution of 2-methylindole in formic acid in a short time becomes deep red, and the addition of water then causes the separation of 2-methylindolyl-2-methylindolidenemethane,



as the *formate*, red needles, m. p. 104°, from which the free *base*, an orange-yellow powder, m. p. 230°, is liberated by ammonium hydroxide; *hydrochloride*; *hydrobromide*, fiery-red needles, m. p. 236°; *perchlorate*, red needles, decomp. at 260°.

D. F. T.

Colours of the Second Order: *holo*- and *meri*-Quinonoid Salts. JEAN PICCARD (*Ber.*, 1913, 46, 1843—1860).—The author has systematically examined the *holo*- and *meri*-quinonoid salts derived from a number of *N*-methyl- and *N*-phenyl-substituted benzidines and *p*-phenylenediamines, and comes to the conclusion that Nietzki's well known rule connecting the increase in the complexity of the molecule with the deepening of the colour from yellow through red and blue to yellowish-green requires modification.

Whereas the *meri*-quinonoid salts derived from benzidine and its diphenyl derivative are coloured respectively blue and yellowish-green, the *meri*-quinonoid salts of tetraphenylbenzidine are yellow.

The author explains this apparent exception as follows: When the complexity of the molecule has been gradually increased to such an extent that the colour has passed successively from yellow to red, blue, bluish-green, and finally yellowish-green, the further increase in the complexity causes a repetition of these colours in the same order; and from analogy with the interference colours the second series are termed colours of the second order.

The *meri*-quinonoid salts of tetraphenylbenzidine thus have a yellow colour of the second order.

Aqueous solution of *meri*-benzoquinonephenyldi-imonium salts are formed by the oxidation of *p*-aminodiphenylamine. The salts are bluish-red and are very unstable, decomposing rapidly in concentrated solution

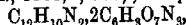
with the formation of emeraldine. The yellow *holo*-quinonoid salts are still less stable.

Solutions of *meri-benzoquinonophenyldimethyldi-imonium* salts are obtained by oxidising *p*-dimethylaminodiphenylamine in acetic acid solution by means of ferric sulphate. They have a blue colour, whilst those of the *holo*-quinonoid salts are red or reddish-yellow according as they are formed by the union of the base with one or two molecules of the acid; a blue *ferricyanide* was prepared by methods similar to those employed by Willstätter and Kalb (A., 1908, i, 475).

Benzoquinonediphenyldi-imine (Bandrowski, A., 1888, 269) combines with NN'-diphenyl-*p*-phenylenediamine to form a quinhedrone base, crystallising in yellow leaflets, m. p. 130—135°; the *holo*-quinonoid salts give red solutions, the *meri*-quinonoid salts greenish-blue; the *holo*-quinonoid *picrate*, $C_{18}H_{14}N_2 \cdot C_6H_3O_7N_3$, forms dark red prisms, the *meri*-quinonoid *picrate*, $C_{80}H_{80}N_4 \cdot 2C_6H_3O_7N_3$, long, green needles.

Solutions of the *meri*-quinonoid salts derived from tetraphenyl-*p*-phenylenediamine are green, whilst those of the *holo*-quinonoid salts are blue; the salts were not isolated.

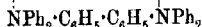
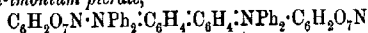
On account of their instability, *holo*-diphenoquinonedi-imonium salts, which are yellow in colour, have hitherto not been isolated (compare Willstätter and Kalb, A., 1908, i, 986); the *picrate*,



is obtained in pointed, brownish-yellow needles by oxidising benzidine dissolved in glacial acetic acid with aqueous chromium trioxide, and adding picric acid to the resulting solution.

The *holo*-quinonoid base derived from diphenylbenzidine is precipitated in an impure condition by the addition of sodium carbonate to aqueous solutions of the salts, which have been described by Kehrman and Micewicz (A., 1912, i, 1020).

The green *holo*-quinonoid and yellow *meri*-quinonoid salts derived from tetraphenylbenzidine are obtained by oxidising the base with the requisite amount of chromium trioxide in glacial acetic acid solution; addition of water and picric acid to these solutions precipitates a very unstable green *holo*- and a yellow *meri*-diphenoquinonoid-tetraphenyldi-imonium *picrate*,



which crystallises in prisms, m. p. 130—134°.

F. B.

holo- and *meri*-Quinonoid Salts of Benzidine. JEAN PICCARD (Ber., 1913, 46, 1860—1862).—A reply to Madelung (A., 1911, i, 678). The author maintains that the *holo*-quinonoid salts of benzidine are yellow and not blue or violet as stated by Madelung.

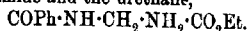
F. B.

Hippenyl *iso*Cyanate [Benzoylaminomethylcarbimide]. THEODOR CURTIUS (J. pr. Chem., 1913, [ii], 87, 513—541).—A recapitulation and extension of earlier work (A., 1896, i, 36). The dibromide of phenylcarbimide, $NPhBr_2CO$, which has been previously obtained in an impure condition by boiling benzoylazoimide with bromine in chloroform solution, is prepared by the direct union of bromine and

phenylcarbimide in chloroform solution at a low temperature. It has m. p. 144°, and if carefully heated sublimes undecomposed. When strongly heated, it loses hydrogen bromide, yielding *p*-bromophenylcarbimide. Benzoylaminoethylcarbimide, $\text{COPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{N}\cdot\text{CO}$, prepared by heating hippurylazoimide in benzene, chloroform, or carbon tetrachloride solution, has m. p. 96–98° according to the rapidity of heating, combines with methyl and ethyl alcohols to form the urethanes previously described (*loc. cit.*), and when boiled with water yields *s*-dibenzoylaminoethylcarbimide together with a substance, m. p. 130°. It combines with benzamide to form *s*-benzoylaminoethylbenzoylcarbimide, $\text{COPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{COPh}$, which has m. p. 221°, and has also been obtained by heating hippurylazoimide with benzamide in xylene solution.

p-Bromohippurylazoimide, prepared from *p*-bromohippurylhydrazide (needles, m. p. 226°) in a similar manner to that employed in the preparation of hippurylazoimide from hippurylhydrazide, crystallises in long, lustrous, silky needles, m. p. 98°, and is converted by boiling in benzene solution into *p*-bromobenzoylaminoethylcarbimide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{N}\cdot\text{CO}$, which crystallises in broad needles, m. p. 114°, unites with hydrogen chloride in benzene solution yielding a hydrochloride, m. p. 235° with previous sintering, and combines with ethyl and methyl alcohols to form the corresponding urethanes of m. p. 174° and 214° respectively.

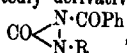
When boiled with water, benzoylazoimide yields only carbanilide, whilst hippurylazoimide gives rise to the following products: carbon dioxide, nitrogen, formaldehyde, hydrazoic acid and its ammonium salt, benzamide, benzoic acid, methylenediamine, ammonium hydrogen hippurate, *s*-dibenzoylaminoethylcarbimide, and *s*-benzoylhippurylmethylenediamine, $\text{COPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{COPh}$, which crystallises in slender, silky needles, m. p. 234°, and is hydrolysed by boiling dilute sulphuric acid to benzoic acid, glycine, ammonia and formaldehyde. In aqueous alcoholic solution, the decomposition of hippurylazoimide is much simpler, the sole products being dibenzoylaminoethylcarbimide and the urethane,



When boiled with water, *p*-bromohippurylazoimide yields di-*p*-bromobenzoylaminoethylcarbimide (Heil, *Diss., Heidelberg*, 1911), hydrazoic acid and its ammonium salt, formaldehyde, *p*-bromobenzamide, and *p*-bromohippuric acid.

F. B.

Benzoylhydrazicarbonyl. OTTO DIELS and HARUKICHI OKADA (*Ber.*, 1913, 46, 1870–1876. Compare A., 1912, i, 511, 918).—Benzoylhydrazicarbonyl reacts with acid chlorides, yielding compounds which are undoubtedly derivatives of the type

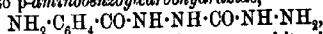


although the formation of metallic salts is best represented on the assumption that the hydrazic compound has the tautomeric formula $\text{OH}\cdot\text{C} < \begin{matrix} \text{N}\cdot\text{COPh} \\ \text{N} \end{matrix}$. Thus, with benzoyl chloride and aqueous potassium

hydroxide it yields dibenzoylhydrazicarbonyl (Stollé and Krauch, this vol., i, 97), which is hydrolysed by fuming hydrochloric acid to benzoic acid and benzoylhydrazicarbonyl, and by dilute sodium hydroxide to *s*-dibenzoylhydrazide, crystallising in lustrous, white needles, m. p. 238°.

Ethyl benzoylhydrazicarbonylcarboxylate, $\text{CO} \begin{smallmatrix} \diagup \text{N} \cdot \text{COPh} \\ \diagdown \text{N} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$, prepared from benzoylhydrazicarbonyl and ethyl chloroformate, forms colourless crystals, m. p. 94°, and is hydrolysed by warm aqueous sodium hydroxide to *ethyl benzoylhydrazinecarboxylate*, $\text{NH} \cdot \text{Bz} \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, which forms lustrous, white plates, m. p. 127°.

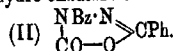
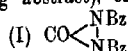
On nitration with sulphuric acid and ethyl nitrate, benzoylhydrazicarbonyl is converted into *p*-nitrobenzoylhydrazicarbonyl. This crystallises in pale yellow leaflets, m. p. 248°, and is reduced by zinc dust and formic acid to *p*-aminobenzoylhydrazicarbonyl, which forms lustrous, silky, colourless leaflets, m. p. 144°, and yields a *sulphate* (decomp. 238°), *hydrochloride*, and *nitrate*. The amino-compound is decomposed by fuming hydrochloric acid at 130° into aniline and hydrazine hydrochloride, and when heated with hydrazine hydrate is transformed into *p*-aminobenzoylcarbohydrazide,



which crystallises from water in lustrous, white leaflets (decomp. 198°), is hydrolysed by hydrochloric acid to *p*-aminobenzoic acid and carbohydrazide, and may also be obtained directly from *p*-nitrobenzoylhydrazicarbonyl by the action of hydrazine hydrate at 80°.

F. B.

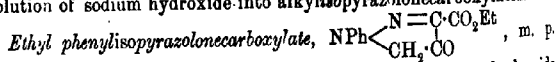
Constitution of Benzoylhydrazicarbonyl. ROBERT STOLLÉ (*Ber.*, 1913, 46, 1993—1994).—The reactions of dibenzoylhydrazicarbonyl (this vol., i, 97) agree with either the hydrazicarbonyl formula (I), which has been assigned by Diels and Okada to benzoylhydrazicarbonyl (preceding abstract), or with the dihydro-oxadiazole formula (II).



The author proposes to combine nitrobenzoylhydrazicarbonyl with benzoyl chloride and benzoylhydrazicarbonyl with nitrobenzoyl chloride, when the compounds should be identical if formula (I) is correct.

J. C. W.

New Series of *iso*Pyrazolones. GEORGES FAVREL (*Compt. rend.*, 1913, 156, 1912—1914).—It has been shown previously that the γ -chloroacetoacetates react with diazo-chlorides to give the α -alkylhydrazones of γ -chloro- $\alpha\beta$ -diketobutyrate (A. 1907, i, 796). The latter are now shown to be converted by the action of aqueous solution of sodium hydroxide into alkylisopyrazolonecarboxylates.



258—260°, obtained by the action of aqueous sodium hydroxide solution on the α -phenylhydrazone of ethyl γ -chloro- $\alpha\beta$ -diketo-

butyrate, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{C}(\text{N},\text{HPh})\cdot\text{CO}\cdot\text{Et}$, crystallises in long, brilliant, faintly yellow needles from boiling alcohol. The *methyl* ester, m. p. 85–87°, forms small, colourless needles.

Ethyl o-tolylisopyrazolonecarboxylate, m. p. 66–68°, forms feebly yellow crystals with difficulty from alcohol. The *methyl* ester, m. p. 178°, forms whitish crystals soluble in methyl alcohol.

Ethyl p-tolylisopyrazolonecarboxylate, m. p. 111–112°, forms yellow needles, and the *methyl* ester is a crystalline, yellow powder, m. p. 218–220°. All these products in alcoholic solution give intense blue colorations with ferric chloride, which are dissipated by acids. They are soluble in weakly alkaline or strongly acid, but not in dilute acid, solutions.

T. A. H.

The Benzoylation of Iminazole [Glyoxaline] Derivatives. OTTO GERNGROSS (*Ber.*, 1913, 46, 1908–1913).—The author finds that the introduction of acyl groups into iminazole and its homologues, which has hitherto been found impossible, can be affected by mixing the acyl chloride with a bimolecular proportion of the base in ether or benzene solution and shaking for a day or so. The hydrogen chloride formed separates in combination with the excess of base and the acylation proceeds smoothly. If necessary the excess of base can frequently be replaced by the corresponding quantity of pyridine. The benzoyl derivatives are very unstable, and in the course of the preparation great care must be taken for the exclusion of traces of moisture.

1-Benzoylglyoxaline, $\begin{matrix} \text{CH}\cdot\text{CH} \\ \text{N}=\text{CH} \end{matrix} > \text{NBz}$, obtained by evaporation of the benzene solution after the above procedure, slowly crystallises in colourless needles, m. p. 19–20°; when exposed to the air it is rapidly converted by moisture into glyoxaline benzoate, plates, m. p. 99–5°.

1-Benzoyl-4(5)-methylglyoxaline, obtained in a similar manner, forms needles, m. p. 54–55°; when treated in alcoholic solution successively with silver nitrate and ammonium hydroxide solutions, a substance crystallising in needles is precipitated. On exposure to the atmosphere, the benzoyl compound is gradually converted into 4(5)-methylglyoxaline benzoate, plates, m. p. 92–93°.

1-Benzoyl-4:5-dimethylglyoxaline, prepared similarly, forms hexagonal plates, m. p. 74–75°. It is affected by the atmosphere.

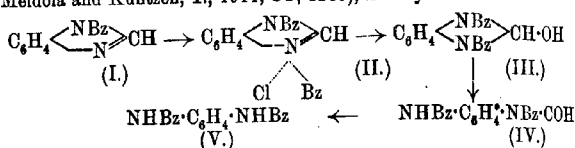
Ethyl 1-benzoyl-4(5)-methylglyoxaline-5(4)-carboxylate forms needles, m. p. 43–45°.

1-Benzoylbenziminazole is obtainable in a similar manner to the previous compounds. Although the simultaneously produced benziminazole hydrochloride can be quantitatively re-converted into the original base, if it is preferred the excess of benziminazole can be replaced by pyridine. The benzoyl derivative is more stable than the preceding ones, for although it is hydrolysed by potassium hydroxide solution, it resists sodium carbonate; it gives a *benzoate*, prisms, m. p. 100°, when mixed in ethereal solution with benzoic acid. The precipitate observed by Bamberger and Berlé (A., 1892, 632) in the action of potassium hydroxide on the benzoyl compound was due to the presence of the alcoholate of 1:3-dibenzoylbenziminazole as impurity.

Benziminazole can be converted into 1-acetylbenziminazole (Bistrzycki and Przeworski, this vol., i, 103) in the same manner.

D. F. T.

The Mechanism of the Scission of Iminazole [Glyoxaline] Derivatives by Benzoyl Chloride and Alkali. OTTO GERNERSS (Ber., 1913, 46, 1913—1924).—The action of benzoyl chloride and an alkali hydroxide on glyoxaline, benziminazole, and their homologues in which the imino-group is unsubstituted, even at 0°, causes scission of the ring with formation of an aliphatic acid and a dibenzoylated diamine (Bamberger and Berlé, A., 1892, 632). If sodium carbonate is used in place of the hydroxide with benzoyl chloride and benziminazole, a formyldibenzoyl-*o*-phenylenediamine can be obtained, and with benzoyl chloride and water in solution in a mixture of benzene and ether, benziminazole gives a dibenzoylbenziminazole-2-ol; these two new products are evidently to be regarded as intermediate steps in the above scission, and the former compound is easily produced from the latter. It is therefore probable that the mechanism of the scission is similar to that of the scission by alkyl haloids and alkali (compare Meldola and Kuntzen, T., 1911, 99, 1283), namely:



for the last three stages can thus be experimentally realised.

When benzoyl chloride is gradually added to an agitated and cooled aqueous solution of sodium carbonate and 4(5)-methylglyoxaline, a substance, tetragonal plates, m. p. 144° (decomp.), probably dibenzoyl-formyl- $\alpha\beta$ -diaminopropylene, is obtained, which, when boiled with water or treated with cold sodium hydroxide solution, undergoes fission into dibenzoyldiamino- $\alpha\beta$ -propylene and formic acid.

Experiments devoted to the isolation of the hypothetical additive compound (formula II above) of benzoylbenziminazole and benzoyl chloride were fruitless, the only new product being a small quantity of benzoylbenziminazole hydrochloride, needles, m. p. 195—200°, which is converted by alkali hydroxides into benziminazole.

1:3-Dibenzoylbenziminazole-2-ol (formula III above) is obtained by vigorously shaking for several hours an equimolecular mixture of benzoylbenziminazole and benzoyl chloride with a half-molecular proportion of water in a mixture of benzene and ether; the substance crystallises in cubes, and above its m. p., 135—140°, gradually resolidifies to needles of formyldibenzoyl-*o*-phenylenediamine (formula IV), m. p. 157°; this substance on further heating also solidifies with evolution of carbon monoxide and formation of dibenzoyl-*o*-phenylenediamine, which finally melts at 306° (decomp.), due to the last stage in the series of changes. The opening of the ring expressed by the formulae III—IV, which is thus caused by heat, can be effected more readily by merely shaking with cold water or warming with methyl

alcohol. Dibenzoylbenziminazole-2-ol when boiled with alcohol or mixed in the cold with alcohol containing hydrogen chloride or even a little benzoyl chloride is converted into the corresponding *ethyl ether*, $C_6H_5 \begin{smallmatrix} \text{NBz} \\ \text{NBz} \end{smallmatrix} \text{OH} \cdot OEt$; when heated with propyl alcohol the ethyl radicle is displaced with formation of the propyl ether. Above its m. p., 139°, the ethyl ether undergoes conversion into an *isomeride*, needles, m. p. 152°, which regenerates the original form on mere recrystallisation. In addition to the above-mentioned method, 1:3-dibenzoylbenziminazolol propyl ether, prisms, m. p. 135–136°, can also be obtained by heating the parent hydroxy-compound with propyl alcohol containing a trace of hydrogen chloride; in the absence of the hydrogen chloride the iminazole ring is forced open.

The action of benzoyl chloride and sodium carbonate solution on benziminazole yields a mixture of formyldibenzoyl-*o*-phenylenediamine and dibenzoyl-*o*-phenylenediamine, which can be separated by making use of the greater solubility of the former in light petroleum or benzene. The formyldibenzoyl-*o*-phenylenediamine on prolonged boiling with water or more quickly with acids or alkalis is converted into formic acid and dibenzoyl-*o*-phenylenediamine.

It is suggested that the opening of the quinoline and benzothiazole rings by benzoyl chloride and alkali (Reissert, A., 1905, i, 925) may be due to a similar series of changes.

D. F. T.

*iso*Hydantoin, 2-Imino-4-ketotetrahydro-oxazole, and its homologues. WILHELM TRAUBE and RICHARD ASCHER (*Ber.*, 1913, 46, 2077–2084).—The reaction of guanidine with esters of α -amino- and α -hydroxy-acids is more complex than with esters of halogen substituted aliphatic acids (Traube, A., 1911, i, 115), in that not only alcohol but ammonia is eliminated, for example, glycine ester yields glycoeyamidine, whilst the esters of the hydroxy-acids yield a reduced oxazole derivative.

When ethyl glycollate is mixed with guanidine in alcoholic solution, heat is developed, and there shortly separates 2-imino-4-ketotetrahydro-oxazole, $NH \cdot C \begin{smallmatrix} \text{NH} \cdot CO \\ \text{O} - CH_2 \end{smallmatrix}$, prisms, m. p. 246–247° (decomp.); hydrochloride, rhombic tablets, m. p. 164° (decomp.); silver salt; copper salt, bright blue. The similarity of this substance to ψ -thiohydantoin, for example, in its hydrolysis by alcoholic hydrogen chloride to 2:4-diketotetrahydro-oxazole, $CO \begin{smallmatrix} \text{NH} \cdot CO \\ \text{O} - CH_2 \end{smallmatrix}$, tablets, m. p. 89–90°, b. p. 173°/11 mm., and by barium hydroxide solution to ammonia, carbon dioxide and glycollic acid, causes the authors to suggest the name ψ - or *iso*-hydantoin for it.

Ethyl lactate also readily reacts with an alcoholic solution of guanidine, giving methyl*iso*hydantoin (2-imino-4-keto-5-methyltetrahydro-oxazole), leaflets, m. p. 226°; hydrochloride, needles. In a manner analogous to the last, this substance undergoes hydrolysis to 2:4-diketo-5-methyltetrahydro-oxazole, a hygroscopic solid, m. p. 44–45° (decomp.), b. p. 156–161°/15 mm.

By an analogous reaction, ethyl mandelate yields *phenylisohydantoin* (2-imino-4-keto-5-phenyltetrahydro-oxazole), crystals, m. p. 256–257° (decomp.); *nitrate*, prismatic crystals, decomp. at 133°; this on warming with dilute hydrochloric acid becomes hydrolysed, producing 2:4-diketo-5-phenyltetrahydro-oxazole, leaflets, m. p. 108°, which is hydrolysed by barium hydroxide solution to mandelic acid, ammonia, and carbon dioxide.

Methyl glycerate reacts readily with guanidine in methyl alcoholic solution, producing *hydroxymethylisohydantoin* (2-imino-4-keto-5-hydroxymethyltetrahydro-oxazole), $\begin{array}{c} \text{NH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{C} \longrightarrow \text{O} \end{array} > \text{CH}\cdot\text{CH}_2\cdot\text{OH}$, prisms, m. p. 197°.

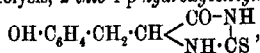
Ethyl aminoacetate and guanidine react vigorously when mixed in equivalent quantities, yielding glycocyamine.

Ethyl ethoxyacetate and ethyl ethoxypropionate both readily enter into reaction with a concentrated alcoholic solution of guanidine, yielding *ethoxyacetylguanidine*, m. p. 162°, and *ethoxypropionylguanidine*, m. p. 196°, respectively. The formation of these compounds is interesting as an indication of the probable intermediate stage in the formation of the isohydantoin derivatives described above, whilst the absence of the second phase of the condensation serves as a confirmation of the structure assumed for the products obtained from the esters of the hydroxy-acids. D. F. T.

Syntheses of Thiohydantoin. II. SHIGERU KOMATSU (*Mem. Coll. Sci. Eng. Kyōto*, 1912, 5, 13–18. Compare A., 1911, i, 683).—The author has modified his interpretation of the mechanism of the reaction whereby thiohydantoin and methylthiohydantoin are formed by the action of potassium thiocyanate on the respective α -amino-acids in the presence of acetic anhydride, and agrees with the view of Johnson and Nicolet (A., 1912, i, 53) that acetyl derivatives of the thiohydantoins are first formed which subsequently undergo hydrolysis. An attempt was made to substitute benzoic anhydride for acetic anhydride, but neither thiohydantoin nor benzoylthiohydantoin was formed.

When potassium thiocyanate and phenyl aminopropionic acid are heated on the water-bath in the presence of acetic anhydride, 2-thio-3-acetyl-4-benzylhydantoin, $\text{CH}_2\text{Ph}\cdot\text{CH} < \begin{array}{c} \text{CO}\text{---}\text{NH} \\ | \\ \text{Nac}\cdot\text{CS} \end{array}$, white needles, m. p. 165–166°, is formed, which, when treated with concentrated hydrochloric acid, is converted into 2-thio-4-benzylhydantoin, white needles, m. p. 175–177°. Desulphurisation by means of mercuric oxide in ammoniacal solution or by digestion with chloroacetic acid in aqueous solution transforms this into 4-benzylhydantoin, platy crystals, m. p. 185–186°, the *silver* salt of which was analysed (compare Wheeler and Hoffman, A., 1911, i, 498).

Potassium thiocyanate and tyrosine when similarly heated with acetic anhydride yield a viscous, yellowish-brown *acetyl* derivative from which, on hydrolysis, 2-thio-4-p-hydroxybenzylhydantoin,

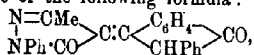


m. p. 203—204° (decomp.), is obtained. Boiling aqueous chloroacetic acid transforms it into 4-*p*-hydroxybenzylhydantoin, m. p. 253—254° (decomp.) [Wheeler and Hoffmann, *loc. cit.*, give m. p. 257—258° (decomp.)].
H. W.

The So called Quinhydrone Salts of the Phenazonium Group. ARTHUR HANTZSCH (*Ber.*, 1913, 46, 1925—1927).—Mainly polemical in reply to Kehrman (this vol., i, 298, 522). The author repeats his statement that the former's view as to a quinhydrone structure for the dark green methylphenazonium iodide is incorrect.

As further evidence he cites the neutral character of the solution of this substance, whilst hydrophenazine salts are almost completely hydrolysed by water; the dilute aqueous alcoholic solution of the iodide has the same greenish-yellow colour as the true phenazonium salts; finally, on grinding with silver nitrate solution or with a suspension of silver sulphate in water, the iodide is converted entirely into a greenish-yellow nitrate or sulphate. These salts from their colour cannot be quinhydrone salts, and they contain no admixed dihydrophenazine salts, because otherwise ether would extract the corresponding dihydro-base from them.
D. F. T.

A Condensation Product from Phenylindanone and 1-Phenyl-3-methyl-5-pyrazolone. GEORGE ROHR and M. TENZER (*J. pr. Chem.*, 1913, [ii], 87, 541—544).—With the object of establishing the constitution of the red acid substance produced by the condensation of 1-phenyl-3-methyl-5-pyrazolone with phthalic anhydride (this vol., i, 297), the authors have attempted to prepare a similar compound, but of simpler constitution, by the condensation of the pyrazolone with benzylidenephthalide. The product formed by fusing the two latter compounds in equimolecular proportions is, however, not a carboxylic acid, but a phenyl nethylpyrazolonylidenephénylindanone of the following formula:



its formation being explained by the transformation of the benzylidenephthalide into 2-phenylindanone, which subsequently condenses with the pyrazolone. This view has been confirmed by the formation of the compound by condensing the pyrazolone with 2-phenylindanone in the presence of anhydrous sodium acetate at 130—135°.

3:1'-Phenyl-3'-methyl-4'-pyrazol-5'-onylidene-2-phenylindanone crystallises in red needles, m. p. 272°, dissolves in alkalis with a deep magenta coloration, and yields an oxime and semicarbazone. With sulphuric acid it develops a dark green coloration.
F. B.

Constitution of Anilopyrine. EZIO COMANDUCCI (*Boll. chim. farm.*, 1913, 52, 436. Compare Comanducci, this vol., i, 296; Zampolli, this vol., i, 296).—Zampolli's criticism is based on errors contained in a preliminary publication of the author, which were corrected before the appearance of Zampolli's paper.
R. V. S.

Iminoindigotins. WALTER MADELUNG (*Ber.*, 1913, 46, 2359—2264. Compare Binz and Lange, this vol., i, 769).—The mono- and di-imines

can be prepared by heating indigotin with the compound of zinc chloride and ammonia.

The monoimine is obtained in almost quantitative yield by gradually introducing indigotin into the ammonia compound fused at 200°, and maintaining at this temperature for half an hour. In the preparation of the di-imine a higher temperature (about 260°) and more prolonged heating are necessary.

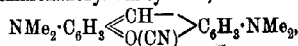
Both imines have the same colour as indigotin, but are much more readily soluble in organic solvents. On reduction with alkaline hyposulphite, the monoimine yields a leuco-compound soluble in alkalis, whilst the di-imine is converted into an insoluble diamine. Advantage is taken of this difference in behaviour to separate the di-imine from the product of the fusion. The leuco-compounds resemble the imines in being readily hydrolysed.

When the monoimine is vatted and the resulting solution, after being heated, submitted to oxidation, a mixture of the monoimine and indigotin is produced. From this the author draws the conclusion that the leuco-compound of the monoimine is present in the vat in the following two forms: $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{C} \begin{smallmatrix} \text{C(NH}_2) \\ \text{NH} \end{smallmatrix} C_6H_4$ and

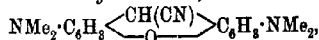
$C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{CH} \begin{smallmatrix} \text{C(NH)} \\ \text{NH} \end{smallmatrix} C_6H_4$. The monoimine crystallises with acetic acid (1 mol.).

Di-iminoindigotin, $C_{16}H_{12}N_4$, forms rosettes of microscopic crystals which decompose above 200°, giving off ammonia. It is more readily soluble in all solvents, and possesses more pronounced basic properties than the monoimino-compound. With mineral acids it forms sparingly soluble salts. F. B.

The Action of Potassium Cyanide on Pyronine and Acridinium Dyes. PAUL EHRLICH and LUDWIG BENDA (*Ber.*, 1913, 46, 1931—1951).—If the red aqueous solution of pyronine-G (tetramethyldiaminoxanthylum chloride) is mixed with aqueous potassium cyanide at the ordinary temperature, a violet-red precipitate of tetramethyldiaminoxanthylum cyanide,



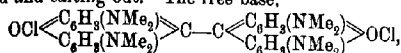
is obtained, which on warming at 65° for ten minutes becomes converted into tetramethyldiamino-9-cyanoxanthem,



which the authors designate pyronine-leucocyanide (compare Hantzsch and Osswald, A., 1900, 1, 256); this substance forms almost colourless needles, m. p. 183°, which rapidly become green when exposed to light; its alcoholic solution on the addition of potassium hydroxide shows a beautiful violet fluorescence. Oxidation of the leuco-compound in hydrochloric acid solution by ferric chloride or lead dioxide, yields *cyanopyronine hydrochloride*, green crystals of metallic lustre; *nitrate*, green, crystalline powder; *chromate*, obtained by effecting the oxidation with dichromate, forms blue flocks; the salts of the base, which has the formula $C_{18}H_{17}ON_3$, give blue aqueous solutions which dye mordanted

cotton and silk, and are reducible to the leuco-compound. With sodium hydroxide solution or ammonium hydroxide in the cold, the salts give a pale blue precipitate, and on acidifying, hydrogen cyanide is evolved, whilst the colour disappears. When boiled with sodium hydroxide solution, complete loss of colour occurs with formation of a precipitate of tetramethyldiaminoxanthone, yellow needles, m. p. 242° (compare Biehringer, A., 1897, i, 73), which in alcohol gives a colourless solution with a violet fluorescence, and in sulphuric acid colourless with a strong blue fluorescence.

If the above tetramethyldiaminoxanthone is reduced by zinc dust and hydrochloric acid in warm aqueous alcoholic solution, *bispyronine*, olive-green crystals, separates as deep blue flocks of a double salt with zinc chloride, from which it is freed by dissolving in very dilute hydrochloric acid and salting out. The free base,



which dissolves in alcohol to a violet solution, and in sulphuric acid to a blood-red, dyes mordanted cotton and silk violet; its violet solution in hydrochloric acid becomes colourless on reduction with zinc dust, but the original coloured substance is regenerated by oxidation with ferric chloride; the base was analysed as the *nitrate*.

3:6-Diamino-10-methylacridinium chloride (compare Benda, A., 1912, i, 651), for which the authors suggest the name *tryptaflavin*, when neutralised with sodium carbonate and treated with potassium cyanide in aqueous solution gives an orange-yellow precipitate of the *cyanide*; on warming the mixture at 75°, the precipitate is converted into pale red 3:6-diamino-5-cyano-10-methyldihydroacridine (compare Kaufmann and Albertini, A., 1909, i, 606), which on oxidation in aqueous hydrochloric acid solution by ferric chloride or potassium dichromate passes into 3:6-diamino-5-cyano-10-methylacridine (*cyanotryptaflavin*), deep green prisms of metallic lustre which give a magenta-red aqueous solution; the aqueous solution on addition of the required mineral acid precipitates the *nitrate*, *hydrochloride*, and *sulphate* respectively, which crystallise in needles; the solutions can be reduced by zinc dust and acid to a colourless substance which regenerates the coloured base on oxidation. The hydrochloride suspended in dilute hydrochloric acid is converted by sodium nitrite into a blue *diazo*-compound resembling diazosafranin. If 3:6-diamino-5-cyano-10-methyldihydroacridine is warmed for forty hours with sulphuric acid, it is oxidised to 3:6-diamino-10-methylacridinium sulphate, together with a *sulphonic acid* of unknown constitution.

When the above diaminocyanomethylacridine is warmed with sodium hydroxide solution, the solution changes its colour from red to brownish-yellow, and 3:6-diamino-10-methylacridone, colourless needles, when pure, m. p. 308° (decomp.), slowly deposits; this dissolves in hydrochloric acid to a deep yellow solution, and in hot water or alcohol to a colourless solution with a violet fluorescence; the hydrochloric acid solution on diazotisation gives a red *diazo*-compound, which couples with *R*-salt to a sparingly soluble red *substance*. Reduction of diaminomethylacridone with sodium amalgam in alcoholic solution and re-oxidation by ferric chloride in acid

solution produces diaminomethylacridinium chloride in poor yield. Reduction in hydrochloric acid by zinc dust, however, gives the zinc chloride double salt, red needles with metallic lustre, of *bistryptaflavin*, $\text{NMeCl} \langle \text{C}_6\text{H}_3(\text{NH}_2) \rangle \text{C} \cdot \text{C} \langle \text{C}_6\text{H}_3(\text{NH}_2) \rangle \text{NMeCl}$.

The formation of this substance is believed to depend merely on the reduction of the pinacone compound which is previously produced (compare Decker and Dunant, A., 1909, i, 433). The addition of nitric acid to a solution of the zincchloride causes the separation of the *nitrate* of the base, orange-red needles; the orange-red aqueous solution of this yields a blue diazo-compound.

3:6-Tetramethyldiamino-10-methylacridinium *p*-toluenesulphonate (used in place of the chloride, that is, acridinium-orange, for convenience) reacts with an aqueous solution of potassium cyanide, giving first an orange-red precipitate of the corresponding *cyanide*, which on warming passes into a black green *substance*; this on oxidation in hydrochloric acid solution by ferric chloride gives *cyano-*

acridinium-orange, $\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \langle \text{C}(\text{CN}) \rangle \text{NMeCl} \text{C}_6\text{H}_3 \cdot \text{NMe}_2$, green crystals soluble in water to a violet colour; *nitrate*, reddish-brown flocks. Reduction of this substance by zinc dust and hydrochloric acid produces a colourless solution, from which oxidation regenerates the original substance as the *chromate* if potassium dichromate is used as oxidising agent. The action of hot potassium hydroxide solution on cyanoacridinium orange causes the formation of *tetramethyldiamino-10-methylacridone*, colourless needles, m. p. 275—276°; *hydrochloride*, yellow needles; the colourless alcoholic solution exhibits a strong violet fluorescence, whilst in sulphuric acid a very strong bluish-green fluorescence is observed. By reduction in dilute hydrochloric acid with zinc dust, tetramethyldiamino-10-methylacridone is converted into *bis-acridinium-orange zincchloride*, red needles with metallic lustre, which, like the previous example, is probably produced by intermediate formation of a pinacone compound; *nitrate*, green crystals with a bronze lustre. The substance is reducible by zinc dust and hydrochloric acid to a yellow solution with green fluorescence, which can be reoxidised to the red solution of the original substance.

Thiopyronine, in an analogous manner, is converted by potassium cyanide into a blue colouring matter.

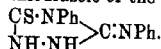
From a consideration of the colours of the products obtained with potassium cyanide and of the colours of the original pyronine or acridine dye, the conclusion is drawn that the grouping $\text{>C} \cdot \text{CN}$ in orthoquinonoid dyes exerts the same effect as a cyclic nitrogen atom >N on the colour; also, that in the cyano-compounds, a rearrangement occurs with formation of a para-quinonoid structure. The latter view is confirmed by experimental results which are to be published later, for example, a striking colour difference exists between 3:6-diamino-10-methylacridinium chloride and its 2:7-dimethyl derivative, the latter of which is structurally prevented from any such rearrangement.

D. F. T.

Products of the Internal Condensation of Hydrazinedithiocarbophenylamide. MAX BUSCH and WILHELM SCHMIDT (*Ber.*, 1913, 46, 2240—2248).—The authors have attempted to prepare a derivative of aminocarbodi-imide, $\text{NH}\cdot\text{C}\cdot\text{N}\cdot\text{NH}_2$, by the removal of hydrogen sulphide from hydrazinedithiocarbophenylamide (*s*-diphenylthiocarbonylhydrazide), $\text{N}_2\text{H}_2(\text{CS}\cdot\text{NHPh})_2$, by heating with mercuric oxide in alcoholic solution. The product consisted, however, of *tetrahydro-*

thiodiazolodianil [*diphenyliminotetrahydrothiodiazole*], $\begin{array}{c} \text{NH}\cdot\text{C}(\text{NPh}) \\ | \\ \text{NH}\cdot\text{C}(\text{NPh}) \end{array} > \text{S}$, which crystallises in lustrous, white leaflets, m. p. 240° , and can also be obtained, together with the anilinothiolthiodiazole described below, by maintaining the hydrazide in a fused condition for a few minutes at a temperature not exceeding 200° .

The thiodiazole has been previously prepared by Walther (A., 1906, i, 831), who assigned to it the formula $\text{NPh}\cdot\text{C}\cdot\text{N}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, whilst Freund and Wischewiansky (A., 1894, i, 97), who obtained it by the action of carbonyl chloride on the hydrazide, considered it to be a phenyliminophenylthiourazole of the constitution

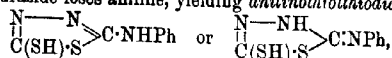


Walther's formula is excluded on account of the absence of additive properties, whilst Freund and Wischewiansky's formula is inadmissible because the substance does not possess distinct acid properties and is not oxidisable to a disulphide.

Evidence in support of the authors' formula is furnished by the behaviour of the thiodiazole on oxidation, whereby a red *azo*-compound, *diphenyliminodihydrothiodiazole*, $\begin{array}{c} \text{N}\cdot\text{C}(\text{NPh}) \\ | \\ \text{N}\cdot\text{C}(\text{NPh}) \end{array} > \text{S}$, crystallising in stout, lustrous, dark violet to brownish-red needles, m. p. 113° , is produced. The oxidation is best carried out by heating an alcoholic solution of the thiodiazole with hydrochloric acid and amyl nitrite.

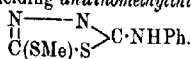
On treatment with nitrous acid the thiodiazole forms a *nitrosoamine*, which is converted by boiling with alcohol or benzene into the above *azo*-compound. That the sulphur atom of the *azo*-compound is contained in the ring is proved by its stability towards mercuric oxide, no action taking place even at 140° .

When boiled with concentrated hydrochloric acid, *s*-diphenylthiocarbonylhydrazide loses aniline, yielding *anilinothiolthiodiazole*,



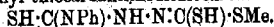
which crystallises in white needles, and has been previously described by Freund and Imgart (A., 1895, i, 400) as a phenyldithiourazole, $\begin{array}{c} \text{NH}\cdot\text{CS} \\ | \\ \text{NH}\cdot\text{CS} \end{array} > \text{NPh}$.

Anilinothiolthiodiazole reacts with methyl iodide and alcoholic potassium hydroxide, yielding *anilinoethylthiolthiodiazole*,



This crystallises in lustrous, colourless, glassy needles or large columns,

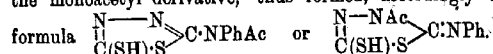
m. p. 127°, and has also been obtained by the removal of hydrogen sulphide from methyl thiocarbaniinodithiocarbazinate,



Anilino benzylthiolthiodiazole, $\text{C}_{15}\text{H}_{13}\text{N}_3\text{S}_2$, prepared in a similar manner, using benzyl chloride, forms pale yellow needles, m. p. 141°. That the above alkyl derivatives contain an imino-group has been shown by the preparation of a *nitrosoamine*, $\text{C}_6\text{H}_5\text{ON}=\text{S}_2$, crystallising in needles, m. p. 84–85°, by the action of nitrous acid on the methyl derivative.

When heated at 100° with benzyl chloride and alcoholic potassium hydroxide, the methyl derivative is converted into *benzylanilino-methylthiolthiodiazole*, $\text{C}_{16}\text{H}_{15}\text{N}_3\text{S}_2$, which forms transparent prisms, m. p. 85°, and yields a *hydrochloride*, m. p. 165°.

The diacetyl derivative of anilinothiolthiodiazole, m. p. 253°, described by Freund and Imgart (*loc. cit.*), readily loses one of its acetyl groups on crystallisation of alcohol. The acetyl group which is so readily removed must be attached to the sulphur of the atom, and the monoacetyl derivative, thus formed, accordingly receives the

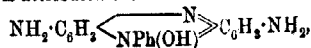


In view of the above results the dithiourazoles described by Freund and Imgart must be considered as amino- or imino-tetrahydrothiodiazoles, whilst the aminothiourazoles are probably di-iminotetrahydrothiodiazoles.

F. B.

Colour Bases of the Quinoneimide Dyes. I. FRIEDRICH KEHRMANN, EM. HAVAS, and EUGÈNE GRANDMOUGIN (*Ber.*, 1913, 46, 2131–2138).—An investigation of the quinoneimide colouring matters, which brings to light certain analogies with the triphenylmethane colours. The occurrence of chemical change was detected spectroscopically.

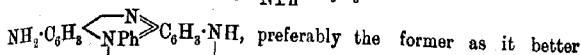
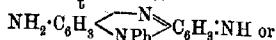
If a solution of safranine in water is treated with alkali and a layer of ether placed on the surface, the two red layers exhibit quite different absorption spectra; the same difference holds for the two layers in the case of the alkylated safranines, but the colours of the ether-soluble bases are in all cases strikingly similar. As the ammonium bases are insoluble in water, the ethereal solutions must contain the imino-base; on shaking with water partial hydration occurs, and a portion of the imino-base passes from the ether as the azonium base and imparts to the water the colour of the original salt. These azonium bases, which conduct the electric current, precipitate ferric hydroxide from ferric solutions, and are generally more stable than the analogous triphenylmethane bases, can also be obtained by the action of moist silver oxide. The equilibrium $\text{NH}_2\text{R} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3\text{R} \cdot \text{OH}$ also shows its effect in the action of much potassium hydroxide, when the excess of hydroxyl ion causes practically all the coloured substance to pass into the ethereal layer as the imino-base. To the substance soluble in water is attributed the structure



corresponding with the salts, for example,



and to the base soluble in ether either



expresses the analogy to the parent substance ammonia in which the valency passes from three to five in salt-formation.

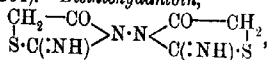
Indamine, the simplest quinoneimide dye, closely resembles safranin in spectrum, thus indicating similarity in constitution, namely, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}$; when shaken with water, however, it does not undergo any appreciable hydration to the corresponding ammonium base, indicating the less basicity of ammonium nitrogen compared with azonium nitrogen.

Tetraethylsafranin, with dilute potassium hydroxide or moist silver oxide, yields only the azonium base, which is insoluble in ether, but as with crystal-violet, on treatment with concentrated alkali, an ethyl radicle is eliminated with formation of triethylsafranin.

With the thiazine dyes, the introduction of successive methyl groups as with safranin, produces an additive effect in the shifting of the absorption band. Methylene-blue like tetraethylsafranin undergoes scission of one and even two methyl groups under the action of potassium hydroxide. The other ethylated thiazines when treated with alkali yield the ether soluble imino-bases, which on shaking with water pass into the thionium bases with simultaneous assumption of the blue colour characteristic of the salts.

D. F. T.

Bisthiohydantoins. GEORG FRERICHS and H. HÖLLER (*Annalen*, 1913, 398, 256—264).—*Bisthiohydantoin*,

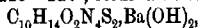


prepared by boiling bisthiocarbamide with aqueous chloroacetic acid, is a colourless, crystalline powder and possesses more pronounced acid properties than thiohydantoin itself. It is easily soluble in alkali hydroxides and carbonates and in aqueous ammonia; the *potassium* salt, $\text{C}_8\text{H}_8\text{O}_2\text{N}_4\text{S}_2 \cdot 2\text{KOH}$, and *barium* salt, $\text{C}_8\text{H}_8\text{O}_2\text{N}_4\text{S}_2 \cdot \text{Ba}(\text{OH})_2$, are crystalline substances. By treatment with methyl or ethyl iodide and *N*/2-potassium hydroxide, an alcoholic solution of bisthiohydantoin is readily converted at the ordinary temperature into *NN*-dimethylbisthiohydantoin, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{S}_2$, m. p. above 270° , colourless needles, or *NN*-diethylbisthiohydantoin, m. p. 224° , neither of which has acidic properties.

Bisthiocarbamide reacts in a similar manner with α -bromopropionic acid and with α -bromobutyric acid. 4 : 4'-Dimethylbisthiohydantoin, $\text{CHMe} \cdot \text{CO} \begin{array}{c} \text{N} \\ \text{S} \cdot \text{C}(\text{NH}) \end{array} \text{N} \cdot \text{N} \begin{array}{c} \text{CO}-\text{CHMe} \\ \text{C}(\text{NH}) \cdot \text{S} \end{array}$, m. p. above 280° (decomp.), forms a *barium* salt, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{S}_2 \cdot \text{Ba}(\text{OH})_2$, an *NN*-dimethyl derivative, m. p.

VOL. CIV. i.

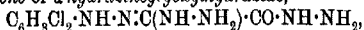
255—256°, and NN-diethyl derivative, m. p. 187°. 4:4'-Diethyl-bisthiodyantoin, m. p. 225—226°, forms a barium salt,



an NN-dimethyl derivative, m. p. 216—217°, and NN-diethyl derivative, m. p. 154°. C. S.

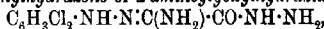
The Anomalies of Uric Acid Solubility (Colloidal Uric Acid). HEINRICH SCHADE and E. BODEN (*Zeitsch. physiol. Chem.*, 1913, 86, 238—243. Compare this vol., i, 404).—Polemical in reply to Lichtwitz (this vol., i, 657). W. D. H.

Action of Hydrazine on the 2:4-Dichlorophenylhydrazones of Ethyl α -Chloro- and α -Amino-glyoxylates and the Decomposition of Phenylazoacetacetamide by Chlorine. Formation of the 2:4-Dichlorophenylhydrazone of α -Chloroglyoxylamide and its Basic Derivatives. CARL BULOW and PETER NEBER (*Ber.*, 1913, 46, 2032—2045. Compare this vol., i, 207).—The 2:4-dichlorophenylhydrazone of α -hydrazinoglyoxylhydrazide,

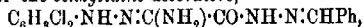


is formed when hydrazine hydrate acts on an alcoholic solution of the 2:4-dichlorophenylhydrazone of ethyl α -chloroglyoxylate under definite conditions which are fully described in the original. It forms straw-yellow leaflets, which rapidly decompose on exposure to air and light, which darken at 155°, and have m. p. 160° (decomp.). It gives an orange-red colour with cold concentrated sulphuric acid which becomes pale, dirty yellow on warming. When warmed with benzaldehyde in alcoholic solution, it yields the corresponding benzylidine derivative, $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}\cdot\text{N}:\text{C}(\text{NH}\cdot\text{N}:\text{CHPh})\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CHPh}$, yellow needles, m. p. 218° (decomp.).

When an alcoholic solution of the 2:4-dichlorophenylhydrazone of ethyl α -aminoglyoxylate is warmed with hydrazine hydrate, the 2:4-dichlorophenylhydrazone of α -aminoglyoxylhydrazide,



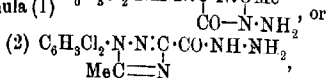
is obtained in long, pale brown needles, m. p. 230° (decomp.). In contrast to the "hydrazidrazone hydrazide" described above, this substance only gives a pale yellow colour with concentrated sulphuric acid, from which the conclusion is drawn that the hydrazino-group attached to the α -carbon atom is the cause of the delicate halochromic property. The presence of the hydrazino-group is established by the preparation of the benzylidine derivative,



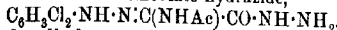
yellow needles.

The 2:4-dichlorophenylhydrazones of α -aminoglyoxylacetethylhydrazide, $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}\cdot\text{N}:\text{C}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{NHAc}$, is formed when a mixture of the 2:4-dichlorophenylhydrazone of ethyl α -aminoglyoxylhydrazide and acetic anhydride is allowed to evaporate at the ordinary temperature. It forms white crystals, m. p. 233°. Its constitution is established by the fact that it does not yield a benzylidine derivative when boiled with benzaldehyde in alcoholic solution, and that it immediately yields a cloudy solution when sodium nitrite solution is added to a solution of it in dilute acid.

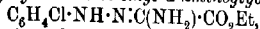
An attempt was made to confirm this conclusion in the following manner. The 2:4-dichlorophenylhydrazone of ethyl α -acetylaminoglyoxylate, $C_6H_3Cl_2 \cdot NH \cdot N : C(NHAc) \cdot CO_2Et$, white needles, m. p. 153° after previous softening, was prepared by the action of cold acetic anhydride on the 2:4-dichlorophenylhydrazone of ethyl α -aminoglyoxylate. When an alcoholic solution of this substance was warmed with hydrazine hydrate, a product, $C_{10}H_9ON_3Cl$, white needles, m. p. 205° , was obtained, which yielded a benzylidene derivative, and had the formula (1) $C_6H_3Cl_2 \cdot NH \cdot N : C : N : CMe$



and was formed from the intermediate hydrazide,



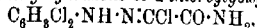
The 4-chlorophenylhydrazone of ethyl α -aminoglyoxylate,



is formed by the action of alcoholic ammonia on the 4-chlorophenylhydrazone of ethyl α -chloroglyoxylate (*loc. cit.*). It has m. p. 158° , and can be distilled without decomposition.

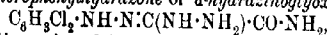
The 2:4-dichlorophenylhydrazone of ethyl α -chloroglyoxylate is best obtained by the action of chlorine on a solution of ethyl phenylazoacetate in acetone. The advantage gained by the substitution of acetone for chloroform (*loc. cit.*) is that the mother liquors from one preparation can be used as solvent for a succeeding preparation, and this procedure has a favourable effect on the yield.

The 2:4-dichlorophenylhydrazone of α -chloroglyoxylamide,

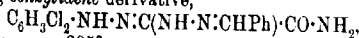


m. p. 232° , is obtained when chlorine is passed into a solution of phenylazoacetamide in glacial acetic acid or alcohol. It is readily soluble in potassium hydroxide. Piperidine converts it into a substance, m. p. $136-136.5^\circ$, which, at a higher temperature, decomposes suddenly with evolution of a volatile oil. With pyridine, it yields pale flesh-coloured needles, m. p. $220-221^\circ$. Investigation of these compounds is not completed. The 2:4-dichlorophenylhydrazone of ethyl α -aminoglyoxylamide, previously described (*loc. cit.*), is more conveniently obtained by the action of cold alcoholic ammonia on the above amide, and has m. p. 176° instead of 170° as previously given. It forms a platinumchloride, crystallising in small, yellow octahedra, reduces boiling gold chloride solution, and gives a mirror with cold ammoniacal silver nitrate.

The 2:4-dichlorophenylhydrazone of α -hydrazinoglyoxylamide,



is obtained by the action of hydrazine hydrate on an alcoholic solution of the 2:4-dichlorophenylhydrazone of α -chloroglyoxylamide. It has m. p. 157° , and gives an orange coloration with concentrated sulphuric acid. With an alcoholic solution of benzaldehyde, it yields the corresponding benzylidene derivative,



yellow needles, m. p. 205° .

In order to determine which of the two amino-groups in the 2:4-di-

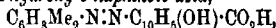
chlorophenylhydrazone of α -aminoglyoxylamide is more loosely held, this substance was energetically treated with an excess of hydrazine hydrate, when the 2:4-dichlorophenylhydrazone of α -aminoglyoxylhydrazide was obtained, thus showing the amino-group of the $-\text{CONH}_2$ radicle to be the more readily replaceable.

H. W.

Azo-dyes Derived from 2-Hydroxy-3-naphthoic Acid.
ANUKUL CHANDRA SIRCAR and EDWIN ROY WATSON (*J. Soc. Chem. Ind.*, 1913, 32, 642—644).—In a previous paper (A., 1912, i, 1037) the authors have described attempts to prepare dyes similar in constitution to benzeneazosalicylic acid, which would possess the same all-round fastness as this dye, but with the colour deepened to red, violet, blue or black. These attempts were not, however, successful as the colour was deepened towards maroon and brown, instead of towards violet and blue as desired. Since many azo-dyes of not more complicated structure possess the desired shades, the authors have examined a list of the well-known azo-dyes prepared from naphtholsulphonic acids, from which they are led to the conclusion that the relative position of the hydroxyl- and chromophore-group is the determining factor in the colour of the dye, the *ortho*-position favouring red, violet, and blue shades, and the *para*-position giving brown shades. A series of dyes have therefore been prepared by coupling diazonium salts with 2-hydroxy-3-naphthoic acid, the hydroxyl group thus being in the *ortho*-position to the azo-group. The shades obtained are very satisfactory, including fiery-red, claret, cherry-red, brownish-purple, bluish-purple and black. The dyeings on chrome-mordanted wool are quite satisfactory as regards fastness to light and acid test, but are not so resistant to soaping, alkalis, and milling as they were expected to be.

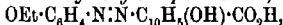
Naphthalene- α -1-azo-2-hydroxy-3-naphthoic acid, prepared from diazotised α -naphthylamine and 2-hydroxy-3-naphthoic acid, forms greenish-red, rhombic prisms, m. p. 236° , whereas Mohlau and Kriebel (A., 1896, i, 242) gave m. p. about 182° .

m-Xylene-1-azo-2-hydroxy-3-naphthoic acid,



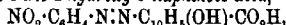
crystallises in deep red needles, m. p. 240 — 242° .

p-Ethoxybenzene-1-azo-2-hydroxy-3-naphthoic acid,



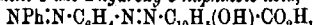
deep red, needle-shaped crystals with green reflex, has m. p. 231° after softening at a somewhat lower temperature.

m-Nitrobenzene-1-azo-2-hydroxy-3-naphthoic acid,



prepared from diazotised *m*-nitroaniline and 2-hydroxy-3-naphthoic acid, separates from nitrobenzene in beautiful red needles, which do not melt at 275° . The corresponding dye from *p*-nitroaniline forms fine hair-like, red needles, which do not melt at 285° .

Benzeneazobenzene-1-azo-2-hydroxy-3-naphthoic acid,



is formed when a diazotised solution of *p*-aminoazobenzene (Hewitt, T., 1909, 95, 1394) is dropped into an alkaline solution of 2-hydroxy-3-naphthoic acid. It crystallises in magenta-red needles with a green reflex and does not melt below 275° .

Diazotised disulphonaphthalene- β -azo- α -naphthylamine combines with an alkaline solution of 2-hydroxy-3-naphthoic acid to yield the sodium salt of disulphonaphthalene- β -azonaphthalene- α -1-azo-2-hydroxy-3-naphthoic acid, $C_{10}H_5(SO_3Na)_2 \cdot N \cdot N \cdot C_{10}H_6 \cdot N \cdot N \cdot C_{10}H_5(OH) \cdot CO_2Na$, which could not be converted into the free acid by boiling with any mineral acid, and forms a black powder. Similarly, sodium benzidine-bis-1-(azo-2-hydroxy-3-naphthoate), $C_{12}H_8[N \cdot N \cdot C_{10}H_5(OH) \cdot CO_2Na]_2$, is prepared by coupling a diazotised solution of benzidine with an alkaline solution of 2-hydroxy-3-naphthoic acid. It forms a green powder from which the corresponding free acid is not obtained by means of boiling mineral acids.

The colorations produced when the dyes are dissolved in alkalis or in concentrated sulphuric acid together with the shades produced on unmordanted or chrome-mordanted wool are also described. H. W.

Azo-colouring Matters of Phenylisooxazolone. ANDRÉ MEYER (*Compt. rend.*, 1913, 156, 1992—1995. Compare A., 1911, i, 341).—As the azo-derivatives previously prepared by the author (*loc. cit.*) contained no salt-forming groups and so were unsuited for dyeing purposes, he has now obtained various compounds chemically suitable for dyes, and has compared them with the corresponding pyrazolone compounds.

Sodium phenylisooxazoloneazobenzene-p-sulphonate,
 $C_6H_5O_2N \cdot N_2 \cdot C_6H_4 \cdot SO_3Na \cdot 2H_2O$,
 golden-yellow spangles, obtained by applying a diazotised solution of sulphamic acid, dyes silk golden-yellow in a bath containing acetic acid.

Sodium phenylisooxazoloneazo-m-xylene-o-sulphonate, an orange, crystalline powder, with $2H_2O$, dyes silk and wool a deep orange-yellow.

Sodium phenylisooxazolone-1-azonaphthalene-4-sulphonate forms orange-brown spangles with $2H_2O$; it dyes silk and wool a reddish-maroon.

Sodium phenylisooxazolone-8-azonaphthalene-2:6-disulphonate, orange crystals with $2H_2O$.

The following substantive dyes were prepared by combining a molecule of a tetrazotised solution of benzidine with a molecule of phenylisooxazolone, and subsequently coupling the free diazo-radicle with a molecule of a phenol or an amine.

Sodium phenylisooxazoloneazodiphenylazonaphthylaminesulphonate, $C_6H_5O_2N \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6(NH_2) \cdot SO_3Na$, obtained by applying naphthionic acid for the second coupling reaction, has a red colour changing to blue on addition of acid; it dyes cotton a scarlet-red.

Sodium phenylisooxazoloneazo-o-ditolylazo-1-amino-8-naphthol-3:6-disulphonate is a reddish-violet powder, changed to bluish-violet by a mineral acid, which dyes a deep violet.

Sodium phenylisooxazoloneazodianisylazo-8-amino-1-naphthol-3:5-disulphonate dyes fabric violet.

Sodium phenylisooxazoloneazodiphenylazosalicylate is a deep brown powder, which dyes cotton orange.

The above dyes are not nearly as fast to light as the pyrazole analogues, the substantive colours being even less stable than the

acid colours mentioned first; ultraviolet radiation affected the colours much more rapidly than ordinary light. The replacement of the imino-group in such compounds by an oxygen atom evidently provokes a weakening towards photochemical influence according with the lessening in stability towards ordinary chemical agents. D. F. T.

Existence of Phenyl-di-imide. STEFAN GOLDSCHMIDT (*Ber.*, 1913, 46, 2300. Compare this vol., i, 768).—In ethereal solution *p*-bromophenyl-di-imide decomposes mainly into *p*-bromobenzene and nitrogen; quinol and a small amount of a colourless, crystalline substance are also produced in the decomposition. F. B.

The Density and Volume of Some Protein Solutions. AMEDEO HERLITZKA (*Zeitsch. Chem. Ind. Kolloid*, 1913, 12, 309).—Polemical (compare Chick and Martin, this vol., i, 40; Herlitzka, A., 1910, ii, 1013; Gayda, A., 1912, i, 399). J. F. S.

Changes in the Physical Condition of Colloids. XV. Electrochemical Investigations on Acid Protein. KATCHIO MANABE and JOH. MATULA (*Biochem. Zeitsch.*, 1913, 52, 369–408).—The investigations are a continuation of those of Pauli. The present authors have been chiefly concerned in the determination of the diminution of hydrogen and chlorine ion concentration when hydrochloric acid is added to carefully dialysed solutions of proteins. The hydrogen ion concentrations were determined in the ordinary manner, with the employment of a shaking electrode devised by Pauli, which is figured in the text. The chlorine ion concentration was determined by shaking the solution under investigation with calomel and mercury, and preparing from this mixture a calomel electrode in the ordinary way. The *E.M.F.* was determined when this was balanced against a calomel electrode containing a definite concentration of potassium chloride ($N/10$ or N). A figure is given in which the *E.M.F.* produced is plotted against the hydrogen ion exponent of the mixture under investigation measured against both N and $N/10$ -potassium chloride. The form of vessel used for these investigations is also figured in the text. In the cases of albumins, or ox-serum, the addition of acids up to a concentration of $0.03N$ is accompanied by an increased binding of the free hydrogen atoms; there are, however, only a relatively small number of chlorine ions bound at the same time, and an equality between the hydrogen and chlorine ions bound is only reached in higher concentrations of the acids. If the difference between the bound chlorine and hydrogen ions is plotted against the hydrochloric acid concentration, it will be found that it gradually reaches a maximum and then falls. The maximum corresponds with the maximum of viscosity of the mixture. These results are in accordance with the theory of Pauli, according to whom an albumin hydrochloride is formed, which dissociates in solution giving rise to albumin and chlorine ions; the high viscosity of the solutions is due to the former. With the addition of increasing amounts of hydrochloric acid, the ionic dissociation of the albumin salt is depressed, and the viscosity

diminishes; an equality between the bound chlorine and hydrogen ions is then also gradually attained. The whole of the hydrogen ions added are never completely bound, and the amount of hydrolytic dissociation of the albumin salt has therefore also been ascertained. For this purpose, the hydrogen ion concentration was determined in an ox-serum solution containing 0.02*N*-hydrochloric acid in undiluted condition and when diluted with twice and four times its bulk of water. From the numbers obtained, it was calculated that the hydrolytic dissociation amounted to 4.4% in the twice diluted solution, and to 15.3% in the four times diluted solution. The results obtained with gelatin are somewhat different to those obtained with albumins. In this case, there is but little binding of the chlorine ions, even in higher concentrations of acids; the explanation offered in this case is, that the chloride is strongly dissociated even in presence of a large excess of acid. This does not, however, explain the diminution of the viscosity in the higher concentrations; it is suggested that the acid causes, in this case, a degradation of the protein. The effect of the addition of salts to the acid protein solutions was also investigated. This addition causes a small increase in the bound hydrogen ions in low concentrations of acids (0.005*N*-HCl). Such an increase cannot, however, be detected with certainty in the higher concentrations. It is assumed that in this case the salt attaches itself to the acid protein by means of accessory valencies. The actions possible in this case are discussed in some detail.

S. B. S.

The Tyrosine Content of Proteins. OTTO FOLIN and WILLEY DENIS (*J. Biol. Chem.*, 1913, 14, 457—458).—Polemical. A reply to Abderhalden and Fuchs (this vol., i, 409). The authors insist that their tyrosine figures are more correct than those hitherto recorded.

W. D. H.

The Factors Concerned in the Solution and Precipitation of Euglobulin. (Miss) HARRIETTE CHICK (*Biochem. J.*, 1913, 7, 318—340).—Re-determination of the isoelectric point of euglobulin shows that it coincides with the point of most rapid agglutination, namely, at a hydrogen ion concentration of about 3×10^{-4} normal. Solution and dispersion of euglobulin by electrolysis is influenced by the nature (especially the valency) of the constituent ions. There are two general types: (1) electrical type of solution in which the dispersion is accompanied by the acquisition of an electric charge by the protein molecules; and (2) molecular type in which the dissolved protein is electrically neutral.

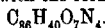
When euglobulin is denaturated by heat, it no longer possesses the property of forming the molecular type of solution. The reaction of acid and alkaline solutions of euglobulin is greatly affected by the addition of electrolytes; the influence of electrolytes in causing precipitation is affected by changes in reaction. Euglobulin in common with caseinogen and vegetable globulins presents an interesting analogy with heat denaturated protein, but differs from it in its capacity to form solutions with electrolytes in which the protein particles are electrically neutral.

W. D. H.

Do Gliadin and Zein Yield Lysine on Hydrolysis? THOMAS B. OSBORNE and CHARLES S. LEAVENWORTH (*J. Biol. Chem.*, 1913, 14, 481—487).—Small quantities of lysine (as picrate) were separated from the hydrolytic products of gliadin from wheat which had been prepared with great care. Zein yielded none. W. D. H.

Phonoporphyrin, a New Degradation Product of Hæmin. OSCAR PILOTY and HERMANN FINKE (*Ber.*, 1913, 46, 2020—2026).—In continuation of their work on the molecular size of hæmin and hæmoglobin (A., 1912, i, 923), the authors have further investigated the reduction of hæmin by hydrogen iodide, and have shown that, in addition to mesoporphyrin, a second substance, *phonoporphyrin*, may be isolated, and that the total weight of products thus obtained is 90% of that theoretically derivable from hæmin. Their previous conclusion that the molecular weight of hæmin is 1303 is thus confirmed. The occurrence of phonoporphyrin among the decomposition products of hæmin seems to have been previously observed by Nencki and Zaleski (A., 1901, i, 434), Zaleski (A., 1903, i, 217), and Fischer and Meyer-Betz (this vol., i, 111), but the substance was not further investigated.

When hæmin is boiled with glacial acetic acid, hydriodic acid (D 1.96), red phosphorus and a little water, and the mixture, after removal of phosphorus, poured into a large bulk of water, a mixture of mesoporphyrin and phonoporphyrin is obtained from which the former may be removed by repeated extraction with large quantities of boiling dilute hydrochloric acid. The residual phonoporphyrin, after purification by solution in sodium hydroxide and precipitation with acetic acid, consists of a dark brown, amorphous powder, analyses of which agree most nearly with the formula $C_{84}H_{36}O_7N_4$ or



It is not obtained when mesoporphyrin is acted on by hydrogen iodide under the above conditions, and hence cannot be formed as an intermediate product of the formation of mesoporphyrin from hæmin.

When boiled with 9% methyl alcoholic hydrochloric acid, phonoporphyrin yields the corresponding *methyl ester*, $C_{86}H_{40}O_7N_4$ or $C_{88}H_{44}O_7N_4$, which forms minute, brown particles showing no distinct crystalline form, and does not soften at 225°. The similarly prepared *ethyl ester*, $C_{88}H_{44}O_7N_4$ or $C_{40}H_{48}O_7N_4$, decomposes at 255°.

Oxidation of phonoporphyrin in sulphuric acid solution with chromic acid gives methylethylmaleinimide and hæmatic acid, $C_8H_9O_4N$.

H. W.

Histone and its Preparation. WALTER H. EDDY (*Biochem. Bull.*, 1913, 2, 419—440).—Histone, obtained by precipitating aqueous extracts of thymus with ammonia, is different from that obtained by saturation with sodium chloride. The former is not soluble in water, and contains more nitrogen; the latter is soluble in water, and contains combined chlorine.

The preliminary use of alcohol to precipitate histone and the other proteins in the glands is preferable to direct water-extraction. Bang's

contention that ammonia does not precipitate histone in the absence of salts is incorrect; their presence, however, facilitates the process.

W. D. H.

Chondroitin-sulphuric Acid. PHÆBUS A. LEVENE and FREDERICK B. LA FORGE (*Biol. Chem.*, 1913, 15, 155—160).—For the first time all the components of this acid were isolated and identified; they are those assumed on indirect evidence by Schmiedeberg, namely, sulphuric acid, acetic acid, glycosamine and glycuronic acid. Schmiedeberg's view of the molecular structure of the molecule needs revision, and the new formula is set out in full. It assumes a glucosidic union of two chondrosin molecules, which explains the reason why chondrosin is a reducing agent, and chondroitin-sulphuric acid is not.

W. D. H.

Sphingomyelin. I. The Presence of Lignoceric Acid among the Hydrolytic Products of Sphingomyelin. PHÆBUS A. LEVENE (*J. Biol. Chem.*, 1913, 15, 153—154).—Thudichum considered that the principal fatty acid in sphingomyelin was isomeric with stearic acid. This is not so; the acid in question has the composition $C_{24}H_{48}O_2$, melts at 81° , and forms an ethyl ester melting at $55\text{--}56^\circ$; hence it is lignoceric acid.

W. D. H.

The Components of Sphingomyelin. PHÆBUS A. LEVENE (*J. Exper. Med.*, 1913, 18, 679—680).—By the hydrolysis of this phosphatide the author has obtained in addition to lignoceric acid (preceding abstract) a base, $C_{15}H_{31}O_2N$, which is isolated in the form of its sulphate, m. p. 225° .

S. B. S.

Myokynine. DANKWART ACKERMANN (*Zeitsch. Biol.*, 1913, 61, 373—378. Compare this vol., i, 181).—Myokynine may be prepared from horse as well as from dog muscle. Myokynine dichloride from the dog muscle has $[\alpha]_D^{20} - 11.09^\circ$, that from horse muscle has $[\alpha]_D^{20} - 13.5^\circ$.

Myokynine can be esterified by means of ethyl alcohol and dry hydrogen chloride; it accordingly contains a carboxyl group. It does not give a pyrrole reaction when distilled with zinc dust. Since an unbranched chain of four carbons in presence of basic nitrogen usually forms pyrrole under these conditions, the presence of such a grouping in myokynine is doubtful.

E. F. A.

Did Von Wittich Antedate Ostwald in the Definition of Enzyme Action? WILLIAM N. BERG (*Biochem. Bull.*, 1913, 2, 441—445).—Quotations from von Wittich's writings of 1872—4 show that his conception of enzyme action was much the same as that of Ostwald. He was probably also the first to describe the adsorption of pepsin by solid proteins, such as fibrin. Abderhalden and others who have utilised the method of recent years have not referred to this.

W. D. H.

Amylolytic Action of Malt and the Reaction of the Medium. HENRI VAN LAER (*8th Inter. Cong. App. Chem.*, 1912, 14, 203—213).—The influence of the addition of varying quantities of acid and alkali on malt extracts of different origin has been studied.

The inhibition resulting from the presence of an excess of acid or alkali is due to the formation of an inactive compound between the enzyme and the acid or alkali. The diminution in the activity of diastase acting in presence of an excess of hydrogen or hydroxyl ions is due to three principal causes: (1) The destruction of a portion of the enzyme—this is non-reversible; (2) the temporary inactivity of part of the enzyme; (3) the increase in the activity due to the disappearance of some of the ions due to the influence of the steadyers (buffers).

Diastase has an amphoteric character, and its specific properties depend on both the acid and basic groups which it contains.

E. F. A.

The Nature of Diastase (Amylase). HENRI VAN LAER (*Bull. Acad. Roy. Belg.*, 1913, 395—451).—A critical examination of previous work on the nature of diastase leads to the conclusion that the enzyme converting soluble starch into maltose is to be regarded as constituted by the association of a colloidal organic nitrogen compound with electrolytes, so allowing the former to act as a catalytic agent, provided always that the reaction of the medium is defined within narrow limits.

Diastase as it exists in cereals differs from the enzyme as used in solution. In the cereal, it is partly present as an insoluble zymogen in combination with protein substances which are capable of attack by pepsin; in solution, the enzyme is free and unaltered either by papain or pepsin.

The organic complement of diastase is digested by a solution of pepsin in hydrochloric acid. It is also modified by phosphotungstic acid like other proteins.

In solutions of diastase the dissolved matter is the more active as the amount of nitrogen in solution increases. The amount of pentosan present bears no relation to the activity of the enzyme. The conclusions are confirmed by extracting powdered diastase with successive equal amounts of water.

In dried preparations the enzyme slowly becomes inactive.

The nitrogen complement of diastase behaves as an amphoteric substance.

The mineral matter is essential for activity, but there is a maximum in the amount of neutral salts, above which any further increase will not cause increased enzyme activity.

At present all the established facts relative to the dynamics of diastatic action are best interpreted on the basis of the properties of emulsoids.

E. F. A.

The Relationship Between the Active and Inactive Condition of a Ferment and its Surface Tension. M. J. GRAMENIZKI (*Biochem. Zeitsch.*, 1913, 52, 142—154).—Taka-diastase

solutions, as the author has already shown, partly recover the activity which has been lost by heating when they are kept. It is now shown that the surface-tensions of the solutions diminish on heating, but again increase on keeping. From these facts, the conclusion is drawn, that there is a connexion between the fermentative activity of a solution and its surface tension.

S. B. S.

Saccharification of Starch by Koji Diastase in Presence of Acids and Salts. F. ANDO (*8th Inter. Cong. App. Chem.*, 1912, 14, 13—24).—Experiments made with an extract of Koji diastase and potato starch in presence of a variety of mineral salts and acids are described. The presence of neutral and acid salts, with the exception of acid calcium phosphate, is up to a certain point favourable to the enzyme. Excess of the salts retards action except in the case of manganese salts.

Alkaline salts, with the exception of potassium phosphate, retard the saccharification. Small quantities of mineral acids accelerate action; organic acids uniformly retard it. Action takes place in solutions of 30% alcohol.

E. F. A.

Some Conditions Affecting the Activity and Stability of Certain Ferments. JOHN H. LONG and WILLIAM A. JOHNSON (*J. Amer. Chem. Soc.*, 1913, 35, 895—913).—It is suggested that for diastatic comparisons, the starch paste should be made from starch prepared in the laboratory from sound ripe potatoes, and subsequently well washed. In experiments in which 0.1 gram of sodium chloride was present in each 100 c.c. of digesting mixture, it was found that amylolytic activity is greatest when about 25 mg. of sodium hydrogen carbonate are also added; sodium hydrogen carbonate in larger quantity retards the action without destroying any of the ferment, whilst the addition of sufficient acid to neutralise the hydrogen carbonate destroys the ferment at once. Glycerol extracts of the pancreas are very stable, but rapidly lose amylolytic power after dilution, especially if kept at 40°; the presence of traces of sodium chloride exerts a considerable protecting effect. Experiments with the glycerol extract indicate that the pancreatic diastase is exceedingly sensitive towards even traces of mineral acid, such as hydrochloric acid, but that salt again exerts a protecting action; the effect of the acid, which is more marked than that of alkali, is probably due to immediate destruction of the enzyme, as neutralisation fails to restore the original activity.

D. F. T.

The Nature of Enzyme Action. III. The Synthetic Action of Enzymes. WILLIAM M. BAYLISS (*J. Physiol.*, 1913, 46, 236—266).—Reactions in the system glycerol, dextrose, glycerol-glucoside and water, as accelerated by emulsin, follow the laws deduced from mass action for an equilibrium in a reversible system, catalysed by a single enzyme. The equilibrium position is the same from whichever end it is approached; the glucoside produced is the β -form, and the same which is hydrolysed by emulsin. The reaction-rate is directly proportional (not linear, how-

ever) to the concentration of the enzyme. The final equilibrium is independent of this concentration.

Brailsford Robertson's "synthesis of paranuclein by pepsin" is not a synthesis, nor is it produced by pepsin; the substance formed is not paranuclein. It is a colloidal precipitation, and has no connexion with enzymic action.

Apparent deviations from the law illustrated should be properly investigated, and the reasons for divergence sought. It is unwise to invent new enzymes to explain difficulties.

W. D. H.

The Lipases Contained in Pancreatic Cysts. KONRAD BOURNOT (*Biochem. Zeitsch.*, 1913, 52, 155—171).—The lipases from the fluids of pancreatic cysts are similar to other animal lipases. The liquids can be filtered through paper without loss of lipolytic activity. This continually diminishes if the liquid is kept, but the residue obtained by evaporation at 20° preserves its lipolytic activity. Acids inhibit the lipolytic action, but alkalis in very low concentrations accelerate it. With small quantities of fluids (0.05—0.2 c.c.) there is a direct proportionality between the amount of enzyme and the fat saponified. For larger quantities of ferment the formulæ of Schütz and Arrhenius hold good. The Schütz law and Arrhenius' equation also agree with the time relations in fat hydrolysis and the oleic acid-glycerol fat synthesis within certain limits. Still better agreement is obtained, however, with the employment of contents calculated from the adsorption isotherm $K = X/E^m$. The maximal hydrolysis of triolein obtained was 93.5%, and the maximal synthesis in the presence of excess of glycerol was 42% of the oleic acid.

S. B. S.

The Lipase of Chelidonium Seeds. KONRAD BOURNOT (*Biochem. Zeitsch.*, 1913, 52, 172—205).—Like the ricinus lipase, the chelidonium lipase is insoluble in water, but is, to a large extent, soluble in the oils extracted by ether from the seeds. It is also somewhat soluble in a mixture of oleic acid and alcohol. Whereas, however, the ricinus lipase acts most readily on addition of acids, the chelidonium ferment acts best in the presence of water alone. Even *N*/50-acetic acid has an inhibitory effect on its action. The maximal hydrolysis obtained was 92—95%. The lipases of ricinus and chelidonium are similar, in that they do not readily hydrolyse the esters of the monohydroxy-alcohols. As the molecular weights of the fatty acids increase, the esters are more rapidly attacked by the chelidonium lipase; thus, isobutyl oleate and amyl palmitate undergo hydrolysis to the extent of 15—33%. The lipase, furthermore, can cause a rapid and almost complete synthesis of the esters of the higher fatty acids, which action is in marked contrast to the less complete hydrolysis of the same esters caused by the ferment. Possibly the larger quantities of water have an inhibitory action when the water of the substrate cannot form an emulsion. The isobutyl oleate synthesis accords with a unimolecular reaction, and there is a direct proportionality between the rate and quantity of enzyme present. The maximal synthesis is 92%. The maximal triolein synthesis is 47—50%. In the latter cases, the same final equilibrium is obtained in synthesis and hydrolysis. The final equilibrium here will depend

on the amount of water present. The seeds can be heated for fifteen minutes at 100° without any very marked deterioration of the ferment.

S. B. S.

Action of Boric Acid on Zymase; Comparison with the Action of Phosphates. HENRI AGULHON (*Compt. rend.*, 1913, 156, 1355—1358).—The author has previously shown (*A.*, 1909, i, 621) that boric acid is remarkably inactive towards diastases in general, and has examined its action on zymase. For this purpose, sucrose or dextrose was mixed with a constant quantity of zymase in the presence of varying amounts of boric acid, the course of the reaction being followed by determining from time to time the loss in weight due to the carbon dioxide evolved. The inhibiting action of boric acid is observable even with only 10 mg. of acid per 100 c.c., whilst with one gram of acid per 100 c.c. fermentation is no longer possible. On the other hand, living yeast derived from the same source is capable of fermenting a portion of the sugar supplied to it even in the presence of boric acid of the concentration 2 in 100, from which it appears that the membrane presents contact of the boric acid with the zymase.

The inhibiting action of boric acid cannot be attributed solely to its acidity, since monosodium phosphate, which possesses the same degree of acidity as boric acid, exerts a slight favouring action. The nature of the electronegative radicle is also important. This is shown by a series of comparative experiments with borax, trisodium phosphate, trisodium citrate, and sodium carbonate, in which only the borax is found to have a marked inhibiting effect. This effect is, however, less than that observed with boric acid, so that it appears that the favouring action of the alkali compensates in some measure the inhibiting action of the electronegative radicle.

H. W.

Physiological Chemistry.

The Work Done by the Lungs at Low Oxygen Pressures. ARCHIBALD V. HILL (*Proc. physiol. Soc.*, 1913, xxvii—xxviii; *J. Physiol.*, 46).—By calculation, from known data, of the work done by the lungs in secreting oxygen (if Haldane's views are accepted) it is found that the work done per minute by the lungs is only 0.8 cal. If therefore the lung cells can secrete oxygen at all, and if they be assumed to possess an "efficiency" in performing the mechanical work of oxygen secretion of only 20%, they should, nevertheless, be well able to perform this work with an activity no greater per gram than that of the body as a whole. W. D. H.

Carbon Dioxide Excretion Resulting from Muscular Work following Forced Breathing. GEORGE O. HIGLEY (*Biochem. Bull.*, 1913, 2, 390—392).—The sudden increase in the excretion of

carbon dioxide after the beginning of work is due to better ventilation of the lungs; the continuation of the increase is due to ventilation of the blood and tissues also. After forced breathing, followed by muscular work, the new rate of excretion is sharply defined; the further increase as the result of work is not so prompt, and comes on gradually. Some differences of detail occur according to the duration of the forced breathing.

W. D. H.

The Influence of Barometric Pressure on the Excretion of Carbon Dioxide in Man. G. O. HIGLEY (*Biochem. Bull.*, 1913, 2, 393—402).—The degree of influence of barometric pressure on the excretion of carbon dioxide differs in different subjects. It is evidently a minor factor, the effect of which is liable to be masked by other influences, diet, exercise, etc.

W. D. H.

The Effect of Altitude on Mesectic Curves. JOSEPH BARCROFT (*Proc. physiol. Soc.*, 1913, xxx—xxxi; *J. Physiol.*, 46).—In subjects at rest living at a high altitude there is a reduced carbon dioxide tension in the blood, and acidosis. These so nearly balance each other that the dissociation curve remains mesectic (that is, normal). This statement is illustrated by the necessary data and calculations.

W. D. H.

The Relation of the Blood-salts to Cardiac Contraction. ERNEST G. MARTIN (*Amer. J. Physiol.*, 1913, 32, 165—183).—Calcium and sodium are not regarded as antagonistic, but each has a definite function. Calcium promotes (as Howell stated) the conversion of stable into unstable energy-yielding material; sodium (as proposed by Lingle) serves as the immediate stimulus to bring about the actual dissociation, and so to initiate the heart-beat. Neither is an exclusive agent; the preparation of dissociable material is much hampered by the accumulation of waste products, and is therefore aided by abundant supplies of oxygen or by sodium carbonate; carbon dioxide in moderate quantities, and perhaps sugar, act as direct stimulants to cardiac tissue much as sodium acts.

W. D. H.

Hæmolysis by Silicic Acid. M. LIEBERS (*Arch. Hygiene*, 1913, 80, 43—55).—In the system blood + silicic acid + complement, hæmolysis often takes place. The silicic acid cannot, however, always replace an ordinary amboceptor. Certain complements show the same complementing action towards sheep corpuscles charged with silica as towards the same corpuscles charged with an ordinary amboceptor. The more coarsely colloidal or turbid solutions of silica cause agglutination, and the blood does not then lûke so readily when treated with the complement. The ordinary immune amboceptor in the original Wassermann reaction cannot be replaced by silica.

S. B. S.

Lipolytic Action of the Blood. FRANCIS H. THIELE (*Biochem. J.*, 1913, 7, 275—286).—Blood and chyle contain an enzyme which can hydrolyse lecithin, but not neutral fat. When blood and chyle fat

are incubated together, the neutral fat forms an absorption compound with the protein, and is then non-extractable by ether. This compound can be broken up by peptic digestion, by alcohol, and by heating. The formation of the complex occurs in the corpuscles; serum has no such effect. It is not due to hæmoglobin, and is probably brought about by an enzyme.

W. D. H.

Variations in Glycæmia during Inanition. HENRY BIERRY and (Mlle.) LUCIE FANDARD (*Compt. rend.*, 1913, 156, 2010—2013).—The authors have already shown (this vol., i, 426) that the injection of adrenaline can induce perturbations in the glycæmia of an animal, and now bring evidence of the considerable effect on the content of sugar in the blood of dogs caused by inanition. The quantity of free sugar is fairly constant for the first twelve days, then may occasionally increase considerably, but finally decreases. The combined sugar, which is liberated on hydrolysis, commences to increase in quantity about the twelfth day and continues to increase until death.

D. F. T.

The Action of the Thromboplastic Substance in the Clotting of Blood. F. W. MACRAE and A. G. SCHNACK (*Amer. J. Physiol.*, 1913, 32, 211—218).—Calcium-free (oxalated) peptone plasma may be made to clot by the addition of calcium-free solutions of thromboplastic substance (kephalin), provided the excess of oxalate is removed by dialysis. The action of the kephalin is demonstrated more easily if some thrombin is added previously to the dialysed oxalate plasma in an amount insufficient in itself to overcome the effect of antithrombin. This result is opposed to the theory of Morawitz that the thromboplastic substance acts as a kinase in conjunction with calcium, but accords with Howell's view that kephalin facilitates clotting by neutralising antithrombin.

W. D. H.

Blood-relationship of Animals as Displayed in the Composition of the Serum-proteins. II. A Comparison of the Sera of Ox, Sheep, Hog, Goat, Dog, Cat, and Guinea-pig with Respect to their Content of Various Proteins. J. HOMER WOOLSEY (*J. Biol. Chem.*, 1913, 14, 433—439).—The following table summarises the average results obtained:

	Percentage of the total proteins in the sera of						
	Ox.	Sheep.	Hog.	Goat.	Dog.	Cat.	Guinea-pig.
"Insoluble" globulin...	8.1	6.4	6.0	6.5	7.7	6.5	4.2
Total globulin	29.0	17.0	36.0	22.0	18.0	30.0	16.0
Total albumin	70.0	82.0	64.0	75.0	81.0	69.0	84.0

W. D. H.

The Activation of Blood-serum. CORNELIS A. PERELHARING (*Zeitsch. physiol. Chem.*, 1913, 85, 341—345).—When blood-serum is kept, its power to coagulate fibrinogen lessens. Morawitz attributes this to a change of thrombin into a metathrombin. Such serum

can be reactivated by adding alkali, and then neutralising; the author advances the view that the loss of activity is due to the development of inhibitory substances, and that these are destroyed by alkali. He also disagrees with Landsberg, who regards the loss of activity as due to adsorption of the thrombin by the serum proteins; and quote experiments to support his view. Among other things proved is the fact that dialysis of the serum removes the inhibitory substance or substances. Activated serum on keeping loses its activity more rapidly than serum which has not been treated with alkali.

W. D. H.

The Digestive Enzymes of Cold- and Warm-blooded Animals. I. The Pepsin of the Hake and Dog. A. RAKOCZY (*Zeitsch. physiol. Chem.*, 1913, 85, 349—371).—The pepsin of hake and dog are not identical, but show the following differences: Hake pepsin digests fibrin, serum protein, and caseinogen well, but it is less active towards edestin, and especially towards egg-albumin and elastin than dog's pepsin. Hake pepsin is adapted to work at a lower acidity than dog's pepsin; there are also differences in milk-curdling power, adsorption by elastin, velocity of action, and in optimum temperature. Hake's pepsin is only slightly inhibited at freezing point.

W. D. H.

The Pepsin-Chymosin Question. WILLEM VAN DAM (*Zeitsch. physiol. Chem.*, 1913, 86, 77—84).—Polemical against Rakoczy's views.

W. D. H.

The Influence of Preliminary Heating on Peptic and Tryptic Digestion. A. H. BIZARRO (*J. Physiol.*, 1913, 46, 267—284).—During peptic digestion, Sørensen's formaldehyde method shows that amino-acid groupings are liberated slowly, and after many days' action the time varies for different proteins. Preliminary heating of egg-white to 120—140° makes subsequent tryptic proteolysis more active; the same is true for fibrin, caseinogen, and beef; but the opposite for gelatin. The amino-acid groupings in tryptic solutions increase after fifteen hours' digestion.

W. D. H.

Pancreatic Digestion. (Miss) GERTRUDE D. BOSTOCK (*Zeitsch. physiol. Chem.*, 1913, 85, 471—492).—A study of the influence of alkali on the partition of nitrogen in the digestion of fibrin by pancreatin shows that the powers to dissolve and to split proteins are two different things. The most favourable degree of alkalinity for protein solution is between 1·2 and 1·8% of sodium carbonate. Protein cleavage is hindered by 0·6% sodium carbonate, but between 0% and 0·3% no differences were noted. An optimum concentration for cleavage was not found. The cleavage during protein tryptic digestion is as unfavourably influenced by 0·6 to 1·2% of sodium carbonate as is protein cleavage during autolysis.

W. D. H.

The Influence of Carbon Dioxide on Chlorine Metabolism. ERNST LAQUEUR and J. SNAPPER (*Biochem. Zeitsch.*, 1913, 52, 44—59).—It has been shown by Hamburger that chlorine passes from the

body fluids into tissue cells when the mixture is treated with carbon dioxide *in vitro*. Experiments carried out with rabbits, which were allowed to inhale air rich in carbon dioxide, failed to reveal a similar action *in vivo*, as no chlorine retention was found to take place after such inhalations, as should be expected if chlorine passed from the blood serum into the formed elements. It is assumed that the body possesses some compensatory mechanism which prevents this from taking place. S. B. S.

The Nitrogen-sparing Action of Salts, Especially of Sodium Acetate, in the Case of Carnivorous Animals. ERNST PESCHBECK (*Biochem. Zeitsch.*, 1913, 52, 275—330).—Numerous experiments are given in detail, in which sodium acetate and other salts were added to basal diets given to dogs, in which the nitrogen balance was, in some cases, complete, in other cases positive, and in still other cases negative. The results of previous experiments were confirmed, which tended to show that sodium acetate causes nitrogen retention, this action being specially marked when the nitrogen balance is a negative one. The salt is without action on the amount of nitrogen excreted in the feces. Sodium citrate, sodium lactate, and magnesium acetate appear to exert a similar action. The author supposes that the action is due to the alkali added, which can be used for neutralisation of acids in the body, instead of the ammonia set free by the deamidisation of the proteins. S. B. S.

[Nitrogenous Metabolism.] EDUARD GRAFE (*Zeitsch. physiol. Chem.*, 1913, 85, 347—348).—Polemical. A final reply to Alderhalden and Lampé (compare this vol. i, 547, 671). W. D. H.

The Normal Protein Metabolism of the Rat. OTTO FOLIN and J. LUCIEN MORRIS (*J. Biol. Chem.*, 1913, 14, 509—515).—The new micro-chemical analytical methods enable small quantities of urine to be dealt with, such as are excreted by the rat. Rat's urine closely resembles that of man. The high percentage of uric acid is remarkable, for the rat's tissues lack the uric acid-forming enzymes, although the liver destroys it. W. D. H.

Intermediary Metabolism of Carbohydrates and Proteins. The Mutual Interconversion of α -Amino-acids, α -Hydroxy-acids, and α -Ketonic Aldehydes. HENRY D. DAKIN and HAROLD W. DUDLEY (*J. Biol. Chem.*, 1913, 14, 555—561; 15, 127—143).—By a suitable choice of experimental conditions it is possible to convert α -amino- and α -hydroxy-acids into α -ketonic aldehydes at low temperatures; lactic acid and alanine, for example, yield methylglyoxal. When methylglyoxal is acted on by enzymes (glyoxalases) found in the body, *D*- and *L*-lactic acid are formed. When given to the glycosuric animal, glyoxal and both lactic acids yield dextrose. Methylglyoxal is therefore believed to be an intermediate product in the mutual interconversion of alanine, lactic acid, and dextrose (compare Proc., 1913, 29, 156). W. D. H.

The Value of Lactose and Galactose after Partial Exclusion of the Liver (Eck's Fistula). LUDWIG DRAUDT (*Arch. exp. Path. Pharm.*, 1913, **72**, 457—474).—After an Eck's fistula the nutritive value of lactose and galactose falls; the liver fails to convert them into glycogen, and the sugars circulate in the blood and leave the body by the urine.

W. D. H.

The Formation of Fat from Carbohydrate. SERGIUS MORGULIS and JOSEPH H. PRATT (*Amer. J. Physiol.*, 1913, **32**, 200—210).—The present observations on dogs confirm the results of others with other animals, that feeding on carbohydrates leads to fat formation with the accompaniment of a high respiratory quotient.

W. D. H.

Fat Absorption. II. Absorption of Fat-like Substances other than Fats. W. R. BLOOR (*J. Biol. Chem.*, 1913, **15**, 105—117).—Neither petroleum hydrocarbons nor unsaponifiable esters (wool-fat) are absorbed. Neither class of compounds is reducible to a water-soluble form in the intestine. Hence it is extremely probable that fats can only be absorbed in water-soluble form, and that saponification is a necessary preliminary to absorption.

W. D. H.

The Absorption of Nitrogenous Products. OTTO FOLIN and WILLEY DENIS (*J. Biol. Chem.*, 1913, **14**, 453—455).—Polemical. A reply to Abderhalden and Lampé (*A.*, 1912, ii, 1189).

W. D. H.

Nutrition of the Embryo-chick III. The Assimilation of Egg-white. HUBERT W. BYWATERS and W. BARRETT ROVE (*Proc. physiol. Soc.*, 1913, xxxiii—xxxiv; *J. Physiol.*, **46**).—During incubation the ratio of albumin to ovomucoid in the white of the egg remains constant. Either the two proteins are absorbed at the same rate or the albumin alone is absorbed, and then fresh albumin is formed from the ovomucoid. The ovomucoid contains the same proportion of carbohydrate throughout. Probably the first explanation is the correct one.

W. D. H.

An Important Chemical Difference between the Eggs of the Sea Urchin and those of the Star-fish. ALBERT P. MATTHEWS (*J. Biol. Chem.*, 1913, **14**, 465—467).—Cholesterol is absent or nearly so in the starfish egg. It could not be found in the eggs of *Asterius forbesii*. It is present in considerable amount in the sea urchin eggs. The phosphatide of the starfish contains about 10% of a reducing sugar in firm combination and also sulphuric acid.

W. D. H.

The Influence of Hypertonic Solution on the Rate of Oxidations in Fertilised and Unfertilised Eggs. JACQUES LOEB and HAROLD WASTENEYS (*J. Biol. Chem.*, 1913, **14**, 469—480).—The unfertilised eggs of sea urchins which have undergone artificial membrane formation die if not treated with a hypertonic solution,

but the solution does not increase the rate of oxidations either in unfertilised or fertilised eggs. Such solutions increase the rate of oxidations in unfertilised eggs if they have not undergone membrane formation. Weak bases added to normal sea-water cause membrane development, and affects the rate of oxidation in unfertilised eggs as when they are added to hypertonic sea-water. Complete cytolysis of the unfertilised eggs by saponin raises the rate of oxidation to the same height as fertilisation, showing that cytolysis of the surface of the egg is the essential feature in fertilisation.

W. D. H.

The Influence of Bases on the Rate of Oxidations in Fertilised Eggs. JACQUES LOEB and HARDOLPH WASTENEYS (*J. Biol. Chem.*, 1913, **14**, 459—464).—Bases influence the rate of oxidations differently in the fertilised and unfertilised eggs of *Strongylocentrotus purpuratus*. Strong bases accelerate this rate in the fertilised egg only if their concentration is over $10^{-3}N$; this suppresses development of the egg. Weak bases accelerate the rate slightly in the fertilised egg. No conclusion as to the seat of oxidation in the egg is warranted.

W. D. H.

Biochemistry of Protozoa. II. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **86**, 33—42).—The parasitic protozoon *Goussia gadi*, which lives in the swim-bladder of certain fishes and also in shellfish, was investigated.

The composition and constants of the fatty substances present show them to be different from those in the host. No sugar or related substance was found. The keratin-like protein in the spore-capsules is free from sulphur and phosphorus. After hydrolysis, lysine, histidine, arginine, tyrosine, glycine, and glutamic acid were separated.

W. D. H.

The Action of Tissues on Hexoses. PHILIPUS A. LEVENE and GUSTAV M. MEYER (*J. Biol. Chem.*, 1913, **15**, 65—68).—Kidney tissue was obtained aseptically, and in its presence dextrose, *d*-mannose, and *d*-fructose were all converted into *d*-lactic acid. The action is the same, but not quite so powerful as that of leucocytes.

W. D. H.

The Biochemical Conversion of Methylglyoxal into Lactic Acid and the Formation of the Different Lactic Acids in Nature. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, **51**, 484—508).—Animal tissue extracts contain an aldehydomutase, which readily converts methylglyoxal into lactic acid. The reaction takes place best when the reaction mixture contains calcium hydrogen carbonate, which prevents the mixture from becoming too acid. This process is carried out in the following way: 1.40 grams of calcium carbonate are added for each 0.72 gram of methylglyoxal present in solution in the organ extract; the former is added, and the liquid is saturated with carbon dioxide before addition of the aldehyde. After remaining in the incubator, the mixture is heated

and filtered, and an aliquot portion is evaporated to a small bulk. Hot alcohol is added, the precipitated substances were filtered off, the filtrate is again evaporated, treated with alcohol, and again evaporated. These processes are continually repeated until no precipitate is produced on addition of alcohol. The amount of lactic acid formed can be estimated by determining the amount of calcium in an aliquot part of the final filtrate; for determination of the rotation the zinc salt can be made from this liquid. Control estimations should be made with the methylglyoxal and tissue extract separately, both of which yield small quantities of a soluble calcium salt when treated by the above process, and a correction can be thus introduced into the result.

The conversion of methylglyoxal into lactic acid is never quantitative, but reaches sometimes 75%. Certain maceration juices of top yeasts are also capable of producing lactic acid from methylglyoxal, but not aqueous extracts of the same. The lactic acid thus produced is inactive. On the other hand, muscle and liver extracts produce the *L*-acid, which is not the naturally occurring form. The theory of the formation of this active form is discussed by the author in some detail. He assumes that by the addition and scission of the elements of water optically active substances can be produced from forms such as methylglyoxal, which are themselves inactive, and that such active substances are formed as intermediary products in various biochemical changes. These views are illustrated by numerous examples and formulæ. S. B. S.

The Preparation from Animal Tissues of a Substance which Cures Polyneuritis in Birds Induced by Diets of Polished Rice. I. EVELYN A. COOPER (*Biochem. J.*, 1913, 7, 268—274).—A fraction rich in the anti-neuritic substance can be precipitated by ether from the fats and lipoids (alcoholic extract) of horse-flesh. The substance is insoluble in alcohol, benzene, chloroform, ether, and ethyl acetate, but is moderately soluble in water. It is absorbed to some extent by animal charcoal, and is destroyed readily by alkali. Quinine and cinchonine exert a temporary curative action in these birds, but lose this power after being heated at 125° for six hours; the effect is regarded as due to traces of the anti-neuritic substance from the cinchona bark. Alcohol given to the birds in small doses does not affect the onset of polyneuritis when a diet of polished rice is taken. This suggests that alcoholic neuritis is not due to a lessened capacity of the body to utilise the anti-neuritic substance. W. D. H.

Lipolytic Action of the Tissues. FRANCIS H. THIELE (*Biochem. J.*, 1913, 7, 287—296).—The tissues possess a true lipolytic enzyme, but, except in the case of the pancreas, it hydrolyses phosphatides and jecorins, but not ordinary fats. It acts in an alkaline or acid medium. There is no evidence of a kinase in the spleen.

W. D. H.

The Influence of Anæsthetics on the Oxydones. FRÉD. BATELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1913, 52, 226—252. Compare Vernon, this vol., i, 220).—The "oxydones" are the insoluble catalysts contained in animal tissues, which accelerate the oxidation of certain substances. Below certain concentrations, anæsthetics have no action on the succinic oxydone; at a certain critical concentration they exert an inhibitory influence, which is not far removed, except in the case of antipyrine, from a limiting concentration at which the ferment becomes quite inactive. Similar phenomena were observed by Vernon in the case of the phenylenediamine oxydone. All anæsthetics have the power of precipitating nucleoproteids from aqueous solution; this precipitation is only marked when a certain critical concentration is reached, and is complete in a slightly higher concentration. These two concentrations, except in the cases of phenol and *o*-cresol, are almost identical with the concentrations necessary for inhibition and complete inactivation of the oxydone. They also vary, in both cases, with the temperature. The influence of the anæsthetics on the activity of the succinic oxydone is not much stronger when they are present during the actual oxidation than when the tissue has been treated by them and then washed. The destruction of the oxydone is therefore an irreversible process. There is, as Vernon has already shown, a parallelism between narcotic action and capacity to destroy oxydones, which is far more marked than the parallelism between the narcotic action and coefficient of distribution between oil and water. There is also a parallelism between the capacity for destroying oxydones and the hæmolytic action, the toxicity, and capillary activity. The authors draw the conclusion that these activities are due rather to actions on the proteins than to the actions on lipoids.

S. B. S.

The Influence of Aldehydes on the Oxydones. FRÉD. BATELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1913, 52, 253—270).—The aldehydes are similar in their action on oxydones to the anæsthetics, the method of action of which is described in the preceding paper. There is a critical concentration at which inhibition is effected, which is not far removed from the limiting concentration of total inactivation. Both vary with the temperature; the destructive action on the oxydones, furthermore, is an irreversible one. These critical and limiting concentrations do not coincide, however, with the incipient and complete precipitation of the nucleoproteins in the case of liver extracts, but, as a general rule, they nearly coincide with the capacity of the aldehyde to form a precipitate with the soluble proteins after acidification with acetic acid. Again, the authors draw the conclusion that the destruction of oxydones is due rather to action on the proteins than to action on the lipoids.

S. B. S.

The Sympathetic System Does Not Possess the Same Chemical Composition as the Axial Nervous Tissue and the Cranial or Spinal Nerves. N. ALBERTO BARBIERI (*Compt. rend.*, 1913, 157, 69—72).—By successive extraction with carbon

disulphide, distilled water, alcohol, ether, and boiling alcohol the author has made a comparative analysis of the tissue of the sympathetic system and of the axial nervous tissue and the cranial and spinal nerves, and finds that the first-named differs in chemical composition from the others. Of its total extract 66% is composed of oil and stearin. It is completely void of nervous serum and of cerebroin and cerebrin.

W. G.

Carbon Dioxide Production in Nerve Fibres. SHIRO TASHIRO (*Amer. J. Physiol.*, 1913, 32, 107—136).—All nerve fibres give off carbon dioxide. A nerve of the spider crab at rest produces 6.7×10^{-7} gram per 10 mg. per ten minutes. The figure for frog's sciatic is 5.5×10^{-7} . The amount is increased in activity to 16×10^{-7} (crab) and 14.2×10^{-7} (frog). This is due to a vital active process, which is reduced by anæsthetics, both in nerves and seeds.

W. D. H.

The Cerebro-spinal Fluid in Nervous Diseases. I. ROBERT V. STANFORD (*Zeitsch. physiol. Chem.*, 1913, 86, 43—50).—The high specific gravity of the cerebro-spinal fluid in cases of progressive paralysis is regarded as of diagnostic importance.

W. D. H.

The Cerebro-spinal Fluid in Nervous Diseases. II. Nitrogen. ROBERT V. STANFORD (*Zeitsch. physiol. Chem.*, 1913, 86, 219—233).—The amount of nitrogen follows the specific gravity; it is increased in progressive paralysis, and in certain other mental diseases, but not so greatly. In epilepsy this is not the case as a rule.

W. D. H.

The Action of Electrolytes on the Heart. GEORGE R. MISES (*J. Physiol.*, 1913, 46, 188—235).—The experiments were made on the frog's heart, simultaneous records of the contractions and of their electrical accompaniment being taken. The character of the electrocardiogram and the changes it undergoes are discussed at length. Among the points of interest noted is that the electrical changes may continue after all movements have ceased, as when calcium is absent from the perfusing fluid. This has already been noticed in the mammal's heart by Locke and Rosenheim.

W. D. H.

The Action of Pituitrin and β -Amino-4-ethylglyoxaline (Histamine) on the Action of the Heart. W. EINIS (*Biochem. Zeitsch.*, 1913, 52, 96—117).—The experiments were made on the isolated hearts of frogs and rabbits. In the rabbit's heart single small doses of pituitrin cause a slight increase in the frequency, larger doses a diminution. Repeated doses also cause a diminution. In hearts brought to a standstill by want of oxygen, pituitrin causes a transient activity. β -Amino-4-ethylglyoxaline causes a diminution of frequency by inhibition of the stimulus. On the mammalian heart pituitrin causes a diminution of frequency, followed by a more or less marked rise; there is a diminution in

the height of contraction, followed by a recovery to the normal, or even higher than the normal. The diminution in the frequency and height of contraction may be ascribed to the chloretone contained in the preparation used. β -Amino-4-ethylglyoxaline causes an increase in the frequency in the mammalian heart to two or three times the normal after a slight preliminary transient diminution. The final value is below normal. It also causes a marked increase in the height of contraction.

S. B. S.

The Action of the Diastatic Ferment on Glycogen within the Cell. III. ERNST J. LESSER (*Biochem. Zeitsch.*, 1913, 52, 471—485).—During the winter months glycogen does not disappear quickly from the liver during incubation of the intact organ. If, however, the organs are ground up so as to destroy the structure, the glycogen rapidly disappears; in fact, it is hydrolysed as rapidly as it is in the intact organs taken from animals during the months of May and June, when the glycogen is labile. The difference is probably due to the difference of the diffusibility of the ferment through the cells, which enables it to come into contact with the glycogen, and not to the presence of blood-diastase, as the same results are obtained with the organs which have been perfused and rendered blood-free, as with the organs directly removed from the body (compare Ivar Bang, this vol., i, 552, 553).

S. B. S.

The Action of Antiglycosuric Medicaments and Liver Glycosuria. III. The Perfusion of the Liver with Blood under the Influence of Different Reagents. ERNST NEUBAUER (*Biochem. Zeitsch.*, 1913, 52, 118—141. Compare A., 1912, ii, 962).—The results were obtained by oncometric experiments on rabbits' livers. An increase of volume of the organ follows the intravenous or subcutaneous injection of adrenaline, and the intravenous injection of the infundibular portion of pituitary body, of strophanthin, of cocaine (after subcutaneous injection of adrenaline), after asphyxia produced by stoppage of the trachea, after faradic stimulation of the central end of the vagus in the neck and the stimulation of the splanchnic. There is contraction or inhibition of expansion of the liver, after intravenous injection of the glandular portion of the pituitary body, after veronal, chloral hydrate, ergotoxin, after venesection, and after stimulation of various kinds of the peripheral end of the vagus. Phloridzin and cocaine have no specific action on the liver volume. Caffeine and diuretin cause repeated alterations in the kidney volume. The liver volume changes run as a rule parallel with the height of the blood-pressure, behaving in this respect like the limbs, but unlike the spleen. Those treatments of the animals which produce hyperglycemia in the liver through vaso-constriction in the splanchnic vessel system cause, generally, expulsion of the sugar, whereas those treatments which antagonise this stasis in the liver, antagonise also glycosuria. The rule is, however, not absolute: diminution of the liver volume produced by insufficient arterial blood supply, for example, can also be accompanied by expulsion of sugar, which also takes place in a stasis produced by anoxybiotic conditions.

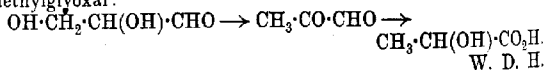
S. B. S.

The Oxidation Products of Cholesterol in the Animal Organism (Portal and Hepatic Veins). V. ISAAC LIFSCHITZ (*Biochem. Zeitsch.*, 1913, 52, 206—213).—The absence of oxy-cholesterol from the liver might be explained, either on the assumption that the liver cannot take up this substance, or that it takes it up from the blood-stream and changes it into other products which do not give the oxycholesterol reactions. From analyses of the blood of the portal and hepatic veins, and of blood which had been artificially perfused through the liver, the second of the above explanations seems to be correct, for the hepatic vein contains less oxycholesterol than the portal vein, and unperfused blood less than perfused blood. S. B. S.

The Effect of Changes in the Circulation of the Liver on Nitrogen Metabolism. SAMUEL A. MATTHEWS and E. M. MILLER (*J. Biol. Chem.*, 1913, 15, 87—104).—After an Eck fistula is established, urea in the urine is largely replaced by ammonia, and toxic effects have been described as the result of increased ammonia in the blood. In the present experiments a large number of the dogs died of inanition, but in some the augmented excretion of ammonia over long intervals did not even produce ill health. Such dogs, however, are susceptible to meat intoxication. In animals which survive a long time the formation of adhesions may bring about a partial return of portal blood to the liver. W. D. H.

Physiology and Pathology of the Kidney Functions. WILHELM BAETZNER (*Archiv exp. Path. Pharm.*, 1913, 72, 309—315).—In experiments on animals it was found contrary to the statements of Bock that in water diuresis a regularly increasing rise in phosphorus elimination takes place. W. D. H.

Action of Leucocytes on Hexoses. IV. The Mechanism of Lactic Acid Formation. PHOEBUS A. LEVENE and GUSTAV M. MEYER (*J. Biol. Chem.*, 1913, 14, 551—554).—The present paper confirms the work of Dakin and Dudley (this vol., i, 565; also corroborated by Neuberg, this vol., ii, 564) on the existence of glyoxalases. In the present experiments bacteria were rigidly excluded. Leucocytes and kidney tissues were used, and produced the conversion of methylglyoxal into *dl*- and *d*-lactic acid. This confirms the view that the formation of *d*-lactic acid from the various *d*-hexoses is conditioned by the intermediate formation of methylglyoxal:



The Physiology of the Thyroid. F. BLUM (*Zeitsch. physiol. Chem.*, 1913, 85, 428—429).—Introductory to a series of papers to follow later. W. D. H.

Self-digestion of the Thymus. ELI K. MARSHALL, jun. (*J. Biol. Chem.*, 1913, 15, 81—84).—In self-digestion of the thymus, the

enzymes present are not capable of decomposing all the nucleic acid within any reasonable length of time; the portion left undecomposed appears to be identical with that prepared from the fresh gland.

W. D. H.

Physical Chemistry of Muscle-plasma. FILIPPO BOTTAZZI (*Biochem. Bull.*, 1913, 2, 379—385).—Muscle-plasma as seen under the ultra-microscope is full of many brilliant, small particles (myosin) and a small number of coarse particles; the latter are composed of fat, glycogen, and nuclear and sarcoplasmic fragments. The liquid portion contains salts, extractives, and protein in true solution. When freed from the granules, the plasma is optically homogeneous, but on adding acid or heating to 55°, true precipitation of a dissolved muscle protein (myoprotein) occurs.

The fine plasma granules are degradation products from the muscular fibrils. They tend to flocculate spontaneously, and the so-called heat coagulation which occurs between 38° and 54° is due to rapid aggregation. Myoprotein is not completely coagulated by heat even at 80°; it is totally precipitated by dialysis. Tables of the composition and physical constants of muscle plasma are appended. The osmotic pressure is high, and the reaction always acid. The maximum production of acid substances occurs soon after the muscles are separated from the body, and it is these which cause the high osmotic pressure. The surface tension is also higher than that of blood-serum.

W. D. H.

Fasting Studies. XI. Composition of Muscle from Fasting Dogs. HENRY C. BIDDLE and PAUL E. HOWE (*Biochem. Bull.*, 1913, 2, 386—389).—The tables given show an increase in water, and a decrease in nitrogen and creatine as a result of fasting. In the heart (one observation only) the nitrogen falls and the creatine rises.

W. D. H.

Carnosine Content of the Muscles of Mammals. MARIE MAUTHNER (*Monatsh.*, 1913, 34, 883—900).—The present investigation was undertaken with the object of deciding whether carnosine is the sole component of the carnosine fraction obtained by Gulewitsch (A., 1900, i, 516) from the muscles of mammals, and also in the hope of discovering an exact method for the estimation of carnosine. The following are the main conclusions:

(i) If a carnosine fraction is obtained from meat extract by addition of lead acetate and silver nitrate, separation of the precipitated matter, addition of silver nitrate and barium hydroxide to the filtrate and decomposition of the precipitate so obtained by means of hydrogen sulphide, it is frequently possible to separate the carnosine in the form of the sparingly soluble, blue, crystalline copper compound described by Gulewitsch. A quantitative separation is, however, never obtained, and there are many indications that, in addition to carnosine itself, a modification or decomposition product of it is often present which does not possess the power of dissolving copper hydroxide.

(ii) Estimations by the picrolonic acid method of the histidine obtained by hydrolysis of carnosine fractions by hydrochloric or sulphuric acids show that 80—90% of the nitrogen present in the latter is contained in the form of carnosine or of a closely allied compound.

(iii) The same result is obtained by the separation of the base from carnosine fractions in the form of a sparingly soluble, yellow, crystalline *picrolonate*, which, according to ultimate analysis and to the amount of picrolonic acid separable from it by addition of hydrochloric acid, is a mono-sodium compound of carnosinedipicronate, $C_{29}H_{29}O_{13}N_{12}Na$.

H. W.

The Occurrence of Alcohol-resistant Carmine-red and Brown-red Pigments in the Skin of Bony Fishes. EMIL BALLOWITZ (*Zeitsch. physiol. Chem.*, 1913, 86, 215—218).—The red pigments referred to occur in the chromatophores, and are distinct from a yellow lipochrome which is soluble in alcohol. W. D. H.

The Presence of Boron in Milk and Eggs. GABRIEL BERTRAND and HENRI AGULHON (*Compt. rend.*, 1913, 156, 2027—2029. Compare A., 1910, ii, 241; 1912, ii, 854; this vol., i, 423).—From the very frequent occurrence of this element in animals and vegetables the authors raise the question as to whether the element may not play, like iron and manganese, an indispensable part (possibly catalytic) in the living cell. They have extended their investigation to milk (human, ass, goat, and cow) and to eggs (fowl, pigeon, wild duck, turkey, and goose), with distinct positive results in each case. Analysis indicates the presence of 0.08, 0.1, and 0.2 mg. of boron in 1 litre of human, ass's, and cow's milk respectively, and 1 mg. of boron in 1 kilogram of dried material from the egg of the fowl, turkey, or goose.

D. F. T.

The Alcohol Content of Milk after Ingestion of Alcohol and under the Influence of Tolerance. WILHELM VÖLTZ and JOHANNES PAECHTNER (*Biochem. Zeitsch.*, 1913, 52, 73—95).—After a short period of toleration the amounts of alcohol appearing in the milk in the case both of cows, and of a woman, who ingested moderate quantities, are practically negligible. When cows are fed on residues from distillation processes, which seldom contain more than 0.1 to 0.3% alcohol, only, at the outside, a few milligrams of alcohol can be ingested daily by infants fed on the milk from such animals, quantities, in fact, which are absolutely without action.

S. B. S.

Action of Hydrogen Peroxide on the Amylase of Human Milk. L. LAGANE (*Compt. rend.*, 1913, 156, 1941—1943).—Starch paste is not liquefied by cow's or goat's milk before or after boiling, but a slight liquefaction occurs with either of these milks in a fresh state in presence of hydrogen peroxide. Fresh human milk, on the contrary, liquefies starch paste, and this action is greatly accelerated in presence of hydrogen peroxide, although the latter

does not enable boiled human milk to effect liquefaction. Similarly, the saccharification of starch paste by fresh human milk takes place more rapidly in presence of hydrogen peroxide, but this action is less marked than the acceleration of liquefaction. Control experiments of various kinds indicate that the acceleration is due to direct action of the peroxide on the amylase, or possibly to indirect action through peroxydases in the milk.

T. A. H.

The Critical Solution Point of Urine. WILLIAM R. G. ATKINS and THOMAS A. WALLACE (*Biochem. J.*, 1913, 7, 219—230).—In normal urines the rise in critical solution-point is about eight times as great as the depression of freezing point. In very dilute urines, and when excess of salts are present, this is greater; in the presence of dextrose or excess of urea it is less. The relationship between the rise of the critical solution temperature and the depression of the freezing point furnishes a useful datum in the examination of urine.

W. D. H.

Toxic Bases in the Urine of Parathyroidectomised Dogs. W. F. KOCH (*J. Biol. Chem.*, 1913, 15, 43—63).—Digested proteins have a very toxic effect after parathyroidectomy; the toxic substances which arise either in intestinal or parenteral digestion pass into the urine, in which secretion several bases were found, among which β -amino-4-ethylglyoxaline, choline, and methylguanidine were identified. In animals in which no feeding occurred, the violent symptoms observed are attributed to disintegration of the body-protein. Histological examination reveals active degeneration of the cell-nuclei. The parathyroid secretion is regarded as concerned with anabolic processes closely related to the building up of nucleins.

W. D. H.

The Chemical Composition of the So-called "Colloidal" Nitrogenous Substances obtained from Human Urine by Precipitation with Zinc Salts. H. THAR and J. BENESLAWSKI (*Biochem. Zeitsch.*, 1913, 52, 435—438).—Salkowski has shown that alcohol produces a precipitation in concentrated human urine which contains nitrogen, is non-dialysable, and was supposed to consist of oxyproteinic acid and similar substances. These same substances can also be obtained by precipitation with zinc sulphate. They have been investigated in greater detail by the authors, who now show that the precipitate contains chiefly uric acid and purine bases, contaminated with small quantities of urea, ammonia, and other constituents of the urine.

S. B. S.

Acapnia and Shock. HENRY H. JANEWAY and EPHRAIM M. EWING (*Biochem. Bull.*, 1913, 2, 403—406).—The conclusion is drawn from experiments on dogs that the reduction of the carbon dioxide of the blood is not an important factor in the production of shock induced by hyper-respiration, but that the essential influence is an interference with the venous return to the heart. In experiments on the intestines, shock is due to manipulation of the gut, and not to

any lessening of carbon dioxide in the blood produced thereby. Aëration of the intestines without the addition of carbon dioxide does not produce shock.

W. D. H.

Beri-beri. VII. The Vitamine Fraction from Yeast and Rice Polishings. CASIMIR FUNK (*J. Physiol.*, 1913, **46**, 173—179).

—The vitamine fraction from yeast was separated into three substances: (1) with formula $C_{24}H_{19}O_9N_5$, (2) with formula $C_{29}H_{23}O_9N_5$, and (3) nicotinic acid. The first substance mixed with the third is stated to have some curative effect on pigeons suffering from polyneuritis.

The vitamine fraction from rice polishings was separated into two fractions: (1) with formula $C_{26}H_{20}O_9N_4$, and (2) nicotinic acid. The deductions as to their curative power are not yet published.

W. D. H.

The Theory of Diabetes. I. Sarcolactic Acid in Diabetic Muscle. ROLLIN T. WOODYATT (*J. Biol. Chem.*, 1913, **14**, 441—451. Compare this vol., i, 559).—Muscles of glycogen-free animals form some sarcolactic acid (about 30% of the normal). This cannot come from glycogen, but must arise from preformed sugar or directly from amino- or fatty acids. The muscles of a severe human case of the disease formed even less than that of fully phloridizised dogs. This suggests an impaired power to dissociate dextrose on the part of the muscles, as they are bathed in an abnormally high quantity of sugar. With D : N (dextrose:nitrogen) ratios of 3·65:1 post-mortem analyses of dog's muscles and livers show no glycogen. With ratios 2·8 or 3·0:1 this is not necessarily the case, and it cannot be assumed that with a constant D:N ratio of this magnitude an animal is free from glycogen.

W. D. H.

The Part Played by Acids in Carbohydrate Metabolism. II. Starvation Diabetes. HERBERT ELIAS and L. KOLB (*Biochem. Zeitsch.*, 1913, **52**, 331—361. Compare this vol., ii, 215).—The object of the investigation was to ascertain whether the diabetes produced by administration of carbohydrates during starvation is due to acidosis. This, from experiments on young dogs, appears to be the case for the following reasons. The starvation diabetes is accompanied by increased acidity of the blood, as determined by Spiro and Pense's method, and by an increased carbon dioxide tension in the alveolar air, as estimated by a modification of Wollberg's technique. The diabetes is always accompanied also by hyperglycemia, which indicates that it cannot be ascribed to renal insufficiency; neither is it due to any action of the suprarenals, as it also occurs after bilateral splanchiotomy. Furthermore, the diabetes is depressed by administration of alkali, which also reduces the blood sugar to the normal. The diabetes appears to be due, therefore, to some disturbance in the intermediary metabolism, and is to a great extent to be ascribed to acidosis.

S. B. S.

The Sugar Consumption in Normal and Diabetic (Depancreated) Dogs after Eviceration. JOHN J. R. MACLEOD and R. G. PEARCE (*Amer. J. Physiol.*, 1913, 32, 184—199).—No differences occur in the consumption of sugar in the muscles and heart of depancreated dogs and normal dogs. This is opposed to the statements of Starling and Knowlton.

W. D. H.

Gluconeogenesis. III. The Fate of *iso*Butyric, *iso*Valeric, and *iso*Hexoic Acids in the Diabetic Organism, with Consideration of the Intermediary Metabolism of Leucine and Valine. A. I. RINGER, EDWARD M. FRANKEL, and L. JONAS (*J. Biol. Chem.*, 1913, 14, 525—538).—In experiments on phloridzinised dogs it was found that *isobutyric* acid and *isobutyl* alcohol give rise to dextrose, probably by undergoing demethylation and so giving rise to normal fatty acids (propionic acid). *iso*Valeric acid does not give rise to dextrose, but to large quantities of acetoacetic acid, acetone, and β -hydroxybutyric acid. *iso*Hexoic acid gives rise to dextrose, probably by demethylation to valeric acid and subsequent oxidation to propionic acid. In certain cases *isobutyric* acid possesses marked antiketogenic properties. It is suggested that *isovaleric* and *isobutyric* acids are normal intermediary products in the katabolism of leucine and valine respectively.

W. D. H.

Gluconeogenesis. IV. The Fate of Succinic, Malic, and Malonic Acids in the Diabetic Organism, with Consideration of the Intermediary Metabolism of Aspartic Acid, Glutamic Acid, Proline, Lysine, Arginine, and Ornithine. A. I. RINGER, EDWARD M. FRANKEL and L. JONAS (*J. Biol. Chem.*, 1913, 14, 539—550).—In phloridzinised dogs, succinic, malic, and perhaps malonic acids give rise to extra dextrose. Succinic acid is an intermediary substance in the metabolism of glutamic acid, ornithine, and proline, which accounts for their conversion into dextrose. Malonic acid may arise in part from the katabolism of aspartic acid; lysine in its catabolism may pass through a glutaric acid stage, which accounts for its non-conversion into dextrose.

W. D. H.

Gluconeogenesis. V. The Rôle of Pyruvic Acid in the Intermediary Metabolism of Alanine. A. I. RINGER, E. M. FRANKEL and L. JONAS (*J. Biol. Chem.*, 1913, 15, 145—152).—In phloridzinised dogs pyruvic acid is capable of yielding extra dextrose in the diabetic organism. In some cases the amount was much less than arises from similar amounts of alanine and lactic acid. Pyruvic acid cannot therefore be considered a necessary intermediary product in the conversion of alanine into lactic acid, and alanine cannot be considered to undergo oxidative deamination.

W. D. H.

The Biochemical Relation between Pyruvic Acid and Dextrose. HENRY D. DAKIN and N. W. JANNEY (*J. Biol. Chem.*, 1913, 15, 177—180).—Results similar to those obtained by Ringer (see preceding abstract).

W. D. H.

The Influence of Thyroid- and Parathyroid-ectomy on Carbohydrate Metabolism. SOICHIRO MIURA (*Biochem. Zeitsch.*, 1913, 51, 423—442).—The onset of alimentary galactosuria in cats is not markedly influenced either by unilateral thyroid or parathyroidectomy. Neither does this exert any influence on the sugar and nitrogen excretion in cases of phloridzin diabetes. Even, therefore, in an animal from which the thyroids and accessory glands have been extirpated, phloridzin causes new sugar formation at the expense of the proteins. Some weeks after the extirpation, however, the sugar/nitrogen ratio increases, as the nitrogen excretion sinks, and is not accompanied with a corresponding decrease of sugar formation. Adrenaline-glycosuria is markedly diminished in animals which have been deprived some weeks before of their thyroid glands and have been treated with phloridzin. S. B. S.

The Influence of Chloral Hydrate on Various Experimental Forms of Hyperglycæmia. AAGE TH. B. JACOBSEN (*Biochem. Zeitsch.*, 1913, 51, 443—462).—In the case of rabbits, chloral hydrate causes hyperglycæmia, and increases hyperglycæmia produced by adrenaline, *piqûre*, and venesection. This increased action is most marked when the chloral exerts a strong narcotising action. In cases where the animals are only slightly influenced by the chloral, it is often impossible to state whether there has been an increase of hyperglycæmia or not. From the results it is impossible to determine whether the *piqûre* hyperglycæmia is due to adrenaline diabetes. S. B. S.

The Influence of Fever on the Elimination of Creatinine. VICTOR C. MYERS and G. O. VOLOVIC (*J. Biol. Chem.*, 1913, 14, 489—508).—Fever increases creatinine excretion; so also in rabbits does artificial hyperthermia; hence the result is due to the rise of temperature which accelerates the normal metabolic processes. In toxic fevers, creatine is also generally found, but usually after the crisis. W. D. H.

Is Narcosis due to Asphyxiation? JACQUES LOEB and HARDOLPH WASTENEYS (*J. Biol. Chem.*, 1913, 14, 517—523).—Chloralhydrate, ethyl urethane, chloroform, and various alcohols produce complete narcosis in the fertilised eggs of the sea urchin, whilst they lower hardly at all the rate of oxidation in the egg. W. D. H.

Transformation of Calomel into Soluble Salts of Mercury in Digestive Media. H. ZILGIER (*Compt. rend.*, 1913, 156, 1863—1864).—Aqueous solutions of lactic acid, ammonia, or previously prepared ammonium lactate do not convert calomel into soluble salts of mercury; if, on the other hand, ammonia is added to a suspension of calomel in water containing lactic acid, a considerable quantity of soluble mercury salts is immediately formed, the amount of which does not increase when the mixture is preserved. A similar result is obtained with nascent ammonium

chloride, although the previously prepared substance is inactive. The soluble salt obtained is probably mercuric chloride. Sodium chloride, whether previously prepared or nascent, is inactive. Similar results are obtained with salts of bismuth, etc., so that probably a general principle is here involved.

In the dog the conversion of calomel into soluble salts of mercury occurs in the stomach only, mercuric sulphate being formed in the intestine. Administration of ammonia in suitable quantity causes a considerable increase in the amount of calomel transformed.

H. W.

The Inactivation of the Hæmolytic Action of Ethyl Alcohol by Normal Serum Albumin. ALBERT FISCHER (*Biochem. Zeitsch.*, 1913, 52, 60—72).—Normal serum inhibits hæmolysis by ethyl alcohol; sodium fluoride serum has a more powerful action in this respect than the serum which separates from a coagulum. Serum albumin also inhibits the hæmolytic action, the process being one of adsorption. Bases are strongly adsorbed by serum albumin, whereas with acids there is a negative adsorption.

S. B. S.

The Mechanism of the Union of Digitalis-like Heart Poisons. VIKTOR WEIZSÄCKER (*Arch. exp. Path. Pharm.*, 1913, 72, 347).—Merck's digitalin acts twenty-five times more strongly than strophanthin. The difference in activity of various preparations depends largely on the amount of active substances in combination, but the depression of cardiac activity depends on the concentration of the toxic molecules in the cell; combinations are formed in the cells.

W. D. H.

The Distribution and Excretion of Digitoxin when Administered Subcutaneously to Bufo vulg. CAMILL LHOTÁK VON LHOTA (*Biochem. Zeitsch.*, 1913, 52, 362—368).—In the case of the toad, digitoxin acts in the first instance as a nerve poison, and only as a heart poison when it is administered in large doses. When administered subcutaneously, it is for the most part absorbed, although a certain portion remains for a long time unabsorbed at the place of injection. The absorbed drug can be detected in the muscular tissue, in the cloacal fluid, and in the urine, in which about 10% of the substance administered is slowly excreted. The greater part of the absorbed drug cannot, however, be detected in the body, and appears to be destroyed. Keller's reaction was employed for the estimation of the digitoxin.

S. B. S.

The Action of Ergotoxine. HENRY H. DALE (*J. Physiol.*, 1913, 46, 291—300).—Ergotoxine does not reverse the motor effects of adrenaline by producing high tonus of plain muscle (blood vessels, uterus); it may even lower tone, and yet replace a motor adrenaline effect by an inhibitory one. Stimulation of the splanchnic nerves, after an adequate dose of ergotoxine, may cause a fall of blood-pressure although the suprarenal glands are removed.

Much of the paper is devoted to a discussion of the detection of sympathetic vaso-dilator nerves. There is no evidence apart from that furnished by the action of ergotoxine for a mixed motor-inhibitory supply to arteries in general. W. D. H.

[Physiological Action of] Certain Derivatives of Quinine. KNUD SCHROEDER (*Arch. expt. Path. Pharm.*, 1913, 72, 361—386).—Towards Infusoria and Plasmodia, monobromoquinine and dibromoquinine are almost twice as strongly active as quinine; and dehydroquinine has about half the activity; the alkaloid, $C_{19}H_{22}O_5N_2Cl_2$, is inactive. These substances act in a similar relative way on bacteria, but not so strongly. Equimolecular doses of the quinine derivatives mentioned have the same antipyretic effect as quinine. They do not affect nitrogeuous metabolism in rats; subcutaneous injection causes local necrosis, the various substances producing this in varying degrees. Dehydroquinine and quinine differ in so much as the vinyl group, $CH:CH_2$, of the quinine is changed into $C:CH$ in the first-named material; this alteration is believed to be responsible for the change in activity. W. D. H.

Action of Morphine on the Circulation. E. ANDERFS (*Arch. expt. Path. Pharm.*, 1913, 72, 331—346).—In both dogs and rabbits morphine causes the heart to slow, although the arterial pressure may be unaltered or even slightly rise. In dogs this is due to central vagus stimulation; in rabbits there is, in addition, a peripheral stimulation due to decrease in negative intrapleural pressure. Curare produces the same effect in rabbits, but in dogs, where it does not alter the intrathoracic pressure, there is no synergic action if both drugs are given together. W. D. H.

[Physiological Action of] Strophanthidin. A. GRÖBER (*Arch. expt. Path. Pharm.*, 1913, 72, 317—330).—Strophanthin acts in rabbits about 3·6 times as toxically as strophanthidin when given intravenously. Death is produced by both drugs by central respiratory paralysis. In minimal lethal doses, strophanthidin acts more quickly and instantaneously, whereas in the case of strophanthin death is preceded by dyspnoea, which lasts for some minutes. On the isolated frog's heart, both poisons act in the same concentration (1 in 1,500,000) in causing standstill of the ventricle. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Oxidation of Petroleum, Paraffin, and Benzene by Bacteria. NICOLAAS L. SÖHNGEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1145—1151).—Although most of the bacteria which oxidise hydrocarbons are unable to decompose fatty acids, some species

belonging to the mycobacteria are able to split fats by the secretion of lipase. Many species, such as *Bacillus fluorescens liquefaciens*, *B. pyocyaneus*, *Micrococcus paraffinae*, etc., were found in soil and canal water, and when cultivated in a medium containing tap water with 0.05% of ammonium chloride, 0.05% of dipotassium phosphate, and 1.0% of the hydrocarbon were able to oxidise the compound with great rapidity. Plate cultures showed the organisms to be extremely widely distributed, and it may rise to about 50,000 per gram of garden soil.

Pure cultures of the paraffin oxidising organisms decomposed, on an average, about 7.5 mg. of petroleum and 4 mg. of paraffin in twenty-four hours at 28° per square centimetre surface of the culture liquid.

H. B. H.

A Comparative Study of the Metabolism of Pneumococcus, Streptococcus, Bacillus lactis erythrogenes, and Bacillus anthracoides. MARY LOUISE FOSTER (*J. Amer. Chem. Soc.*, 1913, 35, 916—919. Compare this vol., i, 684).—A study of the proteolytic power of the various organisms. Two strains of *Pneumococcus* were very different in their power of affecting the protein molecule; increase of temperature from 37° to 40° favoured the reaction to such an extent that with the more active strain the phosphotungstic acid fraction was more than doubled, whilst the monamine fraction is increased in the ratio 6:1. When milk was used as culture medium for *Streptococcus*, *Bacillus lactis erythrogenes*, and *B. anthracoides*, the liquid became alkaline and assumed a red colour and glue-like odour; no indication of lactic acid could be observed. The results indicate the probability of chemical similarity between organisms which morphologically are widely different.

D. F. T.

Mechanism of the Acclimatisation of Yeasts to Formaldehyde. M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1913, 156, 1851—1852).—According to Effront, the acclimatisation of yeasts to formaldehyde is due to the destruction of the latter by an oxidising agent which develops in the yeast, the requisite oxygen being obtained from the air or from substances contained in the mixture; the substance produced by acclimatisation plays the part of selective catalyst, without which oxidation does not occur. The author considers this view to be improbable, and has carried out a series of experiments, in which he finds that (i) formaldehyde actually disappears, (ii) destruction takes place more readily in a medium rich in complex nitrogenous substances; if a poor barley wort is employed and the nitrogenous matter removed by means of tannin, fermentation becomes more difficult in the presence of a constant amount of formaldehyde; fermentation occurs more readily if a large initial quantity of yeast is used; (iii) combustion of formaldehyde is complete since formic acid cannot be detected; (iv) formaldehyde combines almost quantitatively with a wort rich in nitrogenous matter forming a labile compound, from which it can be recovered by energetic treatment. Fermentation, and conse-

quently acclimatisation, of the yeast are more difficult in proportion as the wort is poorer in organic nitrogen, and, with an artificial wort containing only ammonium phosphate, becomes very difficult.

The author is led to the conclusion that formaldehyde loses its antiseptic properties owing to the extreme ease with which it combines with groups containing nitrogen, and that the disappearance of the aldehyde corresponds simply with the consumption of the amino-compound formed by the yeast. H. W.

The Formation of the Higher Alcohols from Aldehydes by Yeasts. I. The Conversion of Valeraldehyde into Amyl Alcohol. CARL NEUBERG and H. STEENBOCK (*Biochem. Zeitsch.*, 1913, 52, 494—503).—It has been already shown by Neuberg and his pupils that keto-acids can be converted by a ferment in yeasts into aldehydes. If these two classes of substances are intermediary products in alcoholic fermentation, it should be expected that the yeasts can convert aldehydes into alcohol. This is now experimentally shown to be possible, and yields of over 80% of the theoretical of amyl alcohol have been obtained from valeraldehyde when this aldehyde is present during alcoholic fermentation. The reaction is apparently a direct reduction, and not a conversion of aldehyde into an equal number of molecules of acid and alcohol by Cannizaro's reaction, as only small quantities of acid could be isolated, and the yield, furthermore, of the alcohol was too large to admit of this explanation. The higher alcohol was separated from the ethyl alcohol by fractional distillation. S. B. S.

The Assimilability of Maltose by Yeasts. A. J. KLEUVER (*Biochem. Zeitsch.*, 1913, 52, 486—493).—It has been shown by Rose that certain yeasts will grow in culture media containing maltose, without producing fermentation, whereas they will not grow in dextrose solutions, although they will produce fermentation with this sugar when added to the medium containing maltose. These results were to a large extent confirmed by more extended researches of Lindner and Saito. The author now shows that certain yeasts will grow in Hayduck's medium containing some preparations of maltose, whereas they will not grow in the presence of maltose obtained from other firms. If, furthermore, the maltose samples which produce growth are purified by recrystallisation, they lose their power of producing growth. The results of Rose, Lindner, and Saito are therefore to be explained by the fact that the maltose they employed was not pure, but contained probably some protein substances derived probably from the diastase used in their preparation. S. B. S.

The Protein Substances of Yeast. PIERRE THOMAS (*Compt. rend.*, 1913, 156, 2024—2027).—The only earlier work of an exact nature on this subject is that of Kossel (*Zeitsch. physiol. Chem.*, 1879, 3, 284; 1880, 4, 290) and of Schröder (A., 1902, i, 730). The author has succeeded, after partial autolysis of yeast, in isolating two protein substances; the first, which from its properties

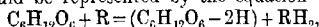
appears to occupy a position between casein and the vitellin of egg-yolk, contains 16.2% nitrogen, 1.8% phosphorus, and 0.38% sulphur; it is soluble in dilute solutions of the alkali hydroxides and carbonates, but is precipitated by acids; rennet causes its coagulation, but less readily than it does caseinogen. If a solution of the protein in 1% sodium hydroxide is maintained, at 37°, the phosphorus passes gradually into the mineral state, the extent of 58% being attained in five days (compare Plimmer and Scott, T., 1908, 93, 1699).

The second substance, for which the author proposes the name *cerevisin*, closely resembles albumin; it is soluble in water, coagulable by heat, and not precipitable by acetic acid; the substance, which contains 16.3% nitrogen, 0.9% sulphur, and a trace of phosphorus, probably due to impurity, gives the usual precipitation and colour reactions.

D. F. T.

Role of Reductase in Alcoholic Fermentation. S. D. Lvov (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 501—532).—Further experiments on the lines of those previously carried out by Palladin and the author (see this vol., i, 684) lead to the following results.

The first stage, or one of the first stages, in alcoholic fermentation consists in the activation of two atoms of hydrogen with the aid of reductase. So far as is at present known, this active hydrogen may be formed either directly from the dextrose or as the result of the ionic dissociation of water; in the latter case the dextrose would be oxidised by the hydroxyl ions, whilst in the former this early stage would be represented by the equation



where R denotes the reductase. The hydrogen fixed temporarily on the reductase is necessary to the further course of normal fermentation. Failure of the distillate to yield the reaction for aldehydes with magenta and sulphurous acid indicates that the formation of aldehydes during the fermentation of sugar, if it actually occurs, is a more complex process than is assumed in Kostytschev's scheme (*A.*, 1912, ii, 589, 860; this vol., i, 323).

Between the reducing and fermentative capacities of yeast strict parallelism is observed; the reductase gives up the hydrogen it fixes to an amount which stands in equimolecular relation to the diminution in yield of the products of fermentation.

A number of auto-fermentation experiments have also been made. The results of these show that the extraction during the process of reduction, of 2 gram-atoms of hydrogen by 1 gram-mol. of methylene-blue, is accompanied by the evolution of an excess of 1 gram-mol. of carbon dioxide. Hence a fermenting medium contains some substance which, in absence of sugar, is capable of liberating 1 mol. of carbon dioxide when the conditions are such that the substance itself loses 2 atoms of hydrogen. This process is found to be enzymic in character, and is one-sided in that no corresponding excess is observed in the yield of alcohol. The excess of carbon dioxide is regarded as resulting from the decomposition of amino-acids, with parallel formation of aldehydes.

The conclusion is drawn that activation of the hydrogen under the influence of reductase is an all-important factor in the processes of fermentation, which are unable to take place in absence of reductase.

T. H. P.

Alcoholic Fermentation of Sugar. EDUARD BUCHNER and KURT LANGHELD (*Ber.*, 1913, 46, 1972).—Sugar was allowed to ferment with expressed or macerated yeast juice in presence of trisodium phosphate or disodium hydrogen phosphate in an extraction apparatus, through which a flow of ether was maintained. The presence of acetaldehyde in the solvent was detected by the formation of the *p*-nitrophenylhydrazone. A similar result was obtained by Kostytschev in the presence of zinc chloride (*A.*, 1912, ii, 589).

J. C. W.

Alcoholic Fermentation. IV. Decomposition of Sugar by Dry Yeast in Presence of Zinc Chloride. S. KOSTYTSCHEV and A. SCHELOUMOV (*Zeitsch. physiol. Chem.*, 1913, 85, 493–506. Compare *A.*, 1912, ii, 589, 860; 1913, i, 323, 434).—When sugar is fermented by yeast preparations in the presence of zinc chloride, the normal series of changes is disturbed and acetaldehyde formed. Parallel with this there is a marked restriction of the production of carbon dioxide. Various zinc salts act in a similar manner, most acetaldehyde being produced in presence of zinc iodide, bromide, or chloride, and less when zinc acetate, carbonate, or phosphate is used.

In the absence of zinc chloride, equal quantities of carbon dioxide and alcohol are obtained on fermentation, but after twenty-four hours about 25% of the sugar decomposed has not been converted into these products; it has probably been used to form hexose phosphate. After forty-eight hours' action, the whole of the sugar is converted into alcohol and carbon dioxide. In parallel experiments in which 0.15 gram of zinc chloride was added per 10 grams of yeast, the sugar is more rapidly decomposed, the fermented part of it being used to form other products. At first the amounts of carbon dioxide and alcohol are equal; after forty-eight hours the production of carbon dioxide is in excess.

When the amount of zinc chloride is doubled, a still larger proportion of the sugar decomposed is not fermented. With 1.2 grams of zinc chloride to 10 grams of yeast, no action takes place.

In a similar manner the addition of 0.5 gram of methylene-blue affects the fermentation. Only two-thirds of the sugar decomposed is fermented, although carbon dioxide and alcohol are produced in equal proportions. The fermentative energy is decreased.

The experiments indicate that the two end-products of fermentation are not formed simultaneously. Alcohol is partly replaced by acetaldehyde.

E. F. A.

Alcoholic Fermentation. V. Decomposition of Protein by Dry Yeast in Presence of Zinc Chloride. S. KOSTYTSCHEV and W. BRILLIANT (*Zeitsch. physiol. Chem.*, 1913, 85, 507–516. Compare preceding abstract).—Generally speaking, external factors act in

an opposite manner towards zymase fermentation and protein decomposition by yeast.

In the absence of sugar, zinc chloride very slightly accelerates the auto-decomposition of dry yeast protein. In the presence of sugar the reverse is the case, the proteolysis being slightly retarded, no doubt owing to the presence of the sugar and the acetaldehyde formed from it. In concentrated sugar solutions the retardation is more marked.

The retardation of the zymase fermentation by zinc chloride is thus not due to acceleration of the antagonistic proteolysis, but to a direct action on the zymase.

E. F. A.

Nitrogen Metabolism in *Aspergillus niger*. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1047—1057).—When grown in nutrient solution containing ammonium salts and dextrose or levulose, the mould is found to give a high nitrogen : carbon ratio. This is attributed not to a simple adsorption of the nitrogen compound, but to its assimilation and immediate transformation into compounds insoluble in hot distilled water.

With increasing age the nitrogen : carbon ratio falls rapidly, and then remains practically constant.

An excretion of ammonia is observed, and this occurs irrespective of the nitrogen compound supplied; nitrate is reduced to ammonia, but not to free nitrogen. The addition of manganese salts increases the velocity of metabolism, whilst the substitution of rubidium for potassium in the nutrient solution is without effect. Where the amount of nitrogen is limited, there did not appear to be any assimilation of atmospheric nitrogen.

H. B. H.

Phosphorus Metabolism in *Aspergillus niger*. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1058—1063).—The ratio of phosphorus to assimilated carbon in old cultures was found to be constant. In the early stages of growth comparatively large quantities of phosphorus are taken up, but, in contradistinction to the same stage in nitrogen assimilation, this phosphorus does not appear to be transformed into organic compounds, such as lecithin or phytin, and can consequently be extracted with hot water. A retardation in spore-formation may be induced by the addition of excess quantities of phosphorus salts.

H. B. H.

Cleavage of Pyromycuric Acid by Mould Enzymes. ARTHUR W. DOX and RAY E. NEIDIG (*Biochem. Bull.*, 1913, 2, 407—408).—Various moulds cleave hippuric acid, and the products can be determined by Sørensen's formaldehyde method. If the synthesis of hippuric acid from benzoic acid in the body is due to an enzyme, the synthesis of corresponding derivatives from substituted benzoic acids may be attributed to the same cause, but there is no reason to suppose that a separate enzyme is necessary for each. This reasoning may be extended to analogous compounds, in which a

heterocyclic replaces the benzene nucleus. In the present experiments, in which pyromycuric acid was subjected to the influence of moulds, the cleavage produced was comparatively small, but this is no evidence that the enzyme is a specific one. W. D. H.

Importance of Oxygen in the Germination of Peas. VI. P. MALTSCHESKI (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 639—664).—The results of experiments on the germination of peas under various conditions bring out the following points.

In the case of living seeds, the action of oxygen in causing germination cannot be replaced by that of methylene-blue. The initial influence of the air in stimulating resting seeds under anaerobic conditions is of great importance, and changes the character of the anaerobic development of carbon dioxide. The alcoholic fermentation produced by seeds under strictly anaerobic conditions is accompanied by another process, which leads to the evolution of carbon dioxide from another source, but furnishes no alcohol. Such process is apparently peculiar to living seeds, and is lacking or, at any rate, greatly enfeebled with dead seeds. In the investigation of the anaerobiosis of seeds, it is essential to deprive the latter of oxygen even in the first stages of steeping. For the initiation of the germination of peas, absorption of atmospheric oxygen is necessary, not merely for supplying the energy liberated by the oxidation of substances existing in the resting seeds, but also for the formation of new compounds. T. H. P.

Assimilation of Iron by Plants. WILHELM VAUBEL (*Chem. Zeit.*, 1913, 37, 737).—Iron and ammonium nitrate interact with production of ferrous oxide, ferric hydroxide, and a small amount of a soluble compound, $\text{Fe}_2\text{O}_3(\text{NO}\cdot\text{NH}_4)_2$, or $\text{Fe}_2\text{O}_3(\text{NO}\cdot\text{NH}_4)_3$ (*ibid.*, 637; Kaufmann, A., 1901, ii, 554). It is suggested that iron is taken up by plants partly in this form. The compound only exists in solution, and decomposes when the solution is evaporated down. According to the concentration, the solution is colourless or dark grey; if yellow, ferric nitrate is present. N. H. J. M.

The Oxidative Formation of Nitrous Acid in Extracts of Plants. ALEXIS BACH (*Biochem. Zeitsch.*, 1913, 52, 418—422).—The author confirms the observation of Mazé, that nitrous acid is formed in plant extracts when exposed to the action of air. The nitrous acid thus produced is spontaneously destroyed. Nitrous acid is formed only in traces, if the extract is first heated. Reasons are given for assuming that nitrous acid is formed from the amino-acids present and not from nitrates, and against the assumption that the formation of iodine from potassium iodide is not due to the presence of nitrous acid, but is due directly to the existence of an oxydase in the tissues. S. B. S.

Relationship of Bases and Mineral Acids in Plant Tissues. GUSTAVE ANDRÉ (*Compt. rend.*, 1913, 156, 1914—1916).—In connexion with Warington's observation (A., 1900, ii, 569), that crops

usually show a deficiency of bases on the assumption that all the nitrogen enters the plant in the form of nitrates, the author points out that this is the case for barley (A., 1912, ii, 675, 803) and for linseed (A., 1913, i, 688), but not for spurrey (*loc. cit.*). In the last case the bases are in excess. T. A. H.

Detection of Urea in Plants. ROBERT ROSSE (*Compt. rend.*, 1913, 156, 1938—1941. Compare A., 1912, ii, 1203; 1913, i, 432).—Some objection might be taken to the work already done on this subject (*loc. cit.*) owing to the fact that the plant preparations in which urea was detected had been concentrated by heat in presence of acetic acid. The author has therefore repeated and extended the work by operating on plant preparations obtained by expression or maceration in the cold. From such products the xanthhydrol derivative of urea is readily precipitated. Urea has thus been detected in the following plants: *Aspergillus niger*, *Penicillium glaucum*, carrot, potato, spinach, endive, chicory, turnip, green haricot, peas, purslane, lettuce, pumpkin, maize grain, and in the embryos of wheat, rye, sunflower, beet, field-bean, lucerne, lentil, lathyrus, grain, pumpkin, horse-bean, dwarf-bean, *Trifolium incarnatum*, and common haricot. Examples of the three methods used in preparing the extracts are given. T. A. H.

The Detection of Formaldehyde in Plants. HEINRICH FINCKE (*Biochem. Zeitsch.*, 1913, 52, 214—225).—For these researches, the Grosse-Bohle reagent for the detection of formaldehyde was employed. This consists of a rosaniline salt in the presence of sulphites and free hydrochloric acid, and is to be distinguished from the ordinary magenta-sulphite solution for detection of aldehydes, by the presence of free mineral acid. It was found by the author to be capable of detecting formaldehyde in the dilution 1 in 500,000, giving with the aldehyde a violet colour. In numerous experiments on plants, no indication of the presence of formaldehyde was obtained with the use of this reagent; furthermore, formaldehyde could not be detected by the reagent after addition to certain living plants. The author draws the conclusion that his investigations throw no light on the correctness or otherwise of Bayer's assimilation hypothesis. S. B. S.

The Reduction Ferments. IV. Vegetable Perhydrazes. ALEXIS BACH (*Biochem. Zeitsch.*, 1913, 52, 412—417).—It has been shown by the author that animal tissues contain a perhydrazase which can reduce nitrates to nitrites in the presence of aldehydes. The existence of a similar vegetable ferment is now demonstrated, which can be obtained from potatoes by extraction with water and filtration of the extract. If this extract is kept under antiseptic conditions (in the presence of sodium fluoride) and in the absence of air, a co-ferment is gradually produced, which can replace the aldehyde in the above-described perhydrazase reaction. The co-ferment which activates the animal perhydrazase, and which is obtained by extraction of animal tissues by hot water, will not

activate the vegetable perhydrase, which also differs from the animal perhydrase in that it will not reduce methylene-blue. It has not yet been found possible to replace the co-ferment in the vegetable perhydrase reaction with amino-acids or keto-acids, and its exact nature is still undetermined.

S. B. S.

Arsenic and Manganese in Young and Old Leaves. P. JADIN and A. ASTRUC (*Compt. rend.*, 1913, 156 2023—2024. Compare A., 1912, ii, 478, 976).—The observation of Pichard (A., 1899, ii, 40) that manganese appears to become concentrated in those parts of a tree which are in vegetative activity, appears to depend for its correctness on the method of analysis.

According to their age, the different organs contain variable proportions of water and of mineral matter. The experimental results indicate that the amounts of arsenic and manganese in the old leaves of various trees examined are decidedly greater than in the young leaves, if the percentage is calculated on the weight of the fresh leaves. The difference becomes less marked if the percentage of the elements is referred to the dried organs, whilst if the percentages are calculated on the ash the case is actually reversed.

D. F. T.

Variation of Carbohydrates in Leaves During Development. E. MICHEL-DURAND (*Compt. rend.*, 1913, 156, 1926—1929. Compare Combes, A., 1909, ii, 426).—The author has determined the dry weight, reducing and non-reducing sugars, glucosides, dextrin, starch, non-nitrogenous extractive matter, amyloids, and cellulose in the leaves of *Fagus sylvatica*, *Ampelopsis hederacea*, and *Betula alba*, at various stages of development during the year. The results for *Betula alba* leaves are quoted in full in the original. The following conclusions are drawn from the whole of the results. There is a general diminution in carbohydrates towards the end of the season. After attaining a maximum dry weight in August to September, the leaves lose weight until and after they fall. The leaves of *Fagus* and *Betula* contain the maximum amount of reducing sugars when yellow; those of *Ampelopsis* when red; these are corresponding states, and after these stages the amount diminishes rapidly. Starch, when it exists, reaches a maximum while the leaves are green, and then diminishes gradually; yellow leaves contain only traces, but in *Fagus* it persists in the dead leaves until these are dry. Amyloids are at a maximum in *Betula* leaves when these are yellow, but in *Ampelopsis* leaves while they are still green. Cellulose diminishes steadily in *Ampelopsis* leaves, but increases steadily in *Betula* leaves. Rain and dew carry off some soluble carbohydrates from dead leaves. The diminution of carbohydrates in leaves as the season's growth proceeds is due partly to migration of these substances into the stem, partly to respiration, and partly to the effect of atmospheric water. The formation of soluble sugars towards the end of the season is favoured by low temperatures.

T. A. H.

Organic Chemistry.

Formation of Methane by Catalysis, Starting with Carbon Monoxide and Water Vapour. Léo VIGNON (*Compt. rend.*, 1913, 157, 131—134. Compare A., 1911, i, 101; ii, 391).—An examination of the effect of the metals iron, nickel and copper, and the oxides of aluminium, magnesium and silicon as catalysts, at temperatures varying from 250° to 1250°, in the formation of methane from carbon monoxide and water vapour. They are all effective, but to a variable degree, nickel being the most active at 600°. The mechanism of the action is different for the various catalysts. In all probability iron and the oxides of aluminium and silicon act through the intermediate formation of a carbide, which is decomposed by the water vapour as fast as it is formed. W. G.

Pyrogenetic Decomposition of the Butadiene Hydrocarbons. HERMANN STAUDINGER, R. ENDLE, and J. HEROLD (*Ber.*, 1913, 46, 2466—2477).—Isoprene when passed through a tube heated at 750° is converted to the extent of 45—55% into a tar, which in appearance and composition closely resembles coal tar, and contains benzene, toluene, naphthalene, α -methylnaphthalene, anthracene, chrysene, etc. The rest of the isoprene is converted into butadiene and into hydrogen, methane, ethylene, or into retort carbon.

At 400° under similar treatment isoprene is partly unattacked, and partly polymerised to unsaturated hydrocarbons—terpenes. Very little gas is formed, but there is some amylene and β -methyl- Δ^2 -butylene produced.

At 600—700° a mixture of unsaturated hydrocarbons results, which no longer contains terpenes, but resembles crude petroleum. At temperatures above 700°, aromatic compounds are formed; at 750° they are almost entirely, and at 800° they are, the only products.

At 700°, but in a vacuum of 20—25 mm., almost half the isoprene remains unchanged. Unsaturated compounds are formed, but no tar.

When isoprene or butadiene is prepared by pyrogenetic reactions it is advisable to work in a vacuum and to cool rapidly if a high yield is desired.

Isoprene is primarily condensed to hydroaromatic compounds. These polymerise further, or condense with isoprene to form substances which decompose into aromatic compounds, the side-chains being eliminated. The formation of the tar from acetylene and ethylene derivatives, which might have been formed primarily by the pyrogenetic decomposition of isoprene, is improbable, since these compounds are not formed at the lower temperatures, or on heating in a vacuum.

Butadiene may originate from the hydroaromatic substances or from amylene.

β -Methyl- Δ^2 -butylene at 750° gives rise to butadiene, but this is obtained in much larger quantity on decomposing amyl alcohol. The alcohol yields relatively little tar; β -methyl- Δ^2 -butylene gives a considerable quantity. In this case also hydrogen is separated from carbon, and there is no scission of carbon linkings with the formation of methane.

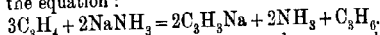
Butadiene also takes part in the formation of the aromatic tar, but it polymerises more slowly than isoprene, and the amount of tar products formed is therefore less.

Dimethylbutadiene behaves just as isoprene does at high temperatures, forming tar and small quantities of butadiene at 800°.

It is considered that the polymerisation of butadiene hydrocarbons plays only a small part in the formation of tar from coal. The tar is mainly formed by the dehydrogenation or decomposition of hydroaromatic substances.

E. F. A.

The Action of Sodium in Liquid Ammonia on the True Acetylenic Hydrocarbons of the Fatty Series, and a Method of Formation of Ethylenic Hydrocarbons. PAUL LEBEAU and MARIUS PICON (*Compt. rend.*, 1913, 157, 137—139).—Sodium in liquid ammonia reacts with the acetylenic hydrocarbons of the fatty series quantitatively, giving the sodium derivative of these hydrocarbons (2 mols.) and the corresponding ethylenic hydrocarbon (1 mol.) according to the equation:



The products of the reaction are pure, and no secondary reactions were noticed.

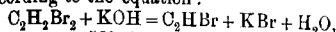
W. G.

Ethylenic Isomerism of *s*-Dibromoethylene. H. VAN DE WALLE (*Bull. Soc. chim. Belg.*, 1913, 27, 209—217).—Crude *s*-dibromoethylene is best obtained in quantity by the action of zinc on an alcoholic solution of tetrabromoethane. It boils at 108—112°, and the two isomerides cannot be separated by fractional distillation on account of the spontaneous reversion of the different fractions to the equilibrium mixture. Attempts to separate them by fractional solidification and also by fractional precipitation by water of a solution of the crude bromo-derivative in acetic acid were unsuccessful. Their isolation can be effected, however, by taking advantage of the fact that each isomeride forms a binary mixture with alcohol. By repeated fractionation of a solution of the crude substance in absolute ethyl alcohol with careful exclusion of moisture, two binary mixtures can be isolated. The first of these has b. p. 75.6—75.9°/760 mm., and contains 64% of *s*-dibromoethylene, m. p. -6.5°. The second has b. p. 77.7—78°/760 mm., and contains 32.5% of *s*-dibromoethylene, m. p. -53°. The pure compound, m. p. -6.5°, has b. p. 108°, D_4^{15} 2.2667, $n_D^{17.5}$ 1.54563, $n_D^{17.5}$ 1.55054, $n_D^{17.5}$ 1.57381, whilst the other isomeride has b. p. 112.5°, $D_4^{17.5}$ 2.2846, $n_D^{17.5}$ 1.53837, $n_D^{17.5}$ 1.53791, $n_D^{17.5}$ 1.54312, $n_D^{17.5}$ 1.54256, $n_D^{17.5}$ 1.55406. Slight errors are probably involved in the determination of the density owing to rapid isomerisation which occurs with such facility that an equilibrium mixture is formed in the course of a few hours. On exposure to air and moisture, the dibromo-compounds are readily decomposed with evolution of hydrogen bromide.

The equilibrium mixture of the two isomerides has $D_4^{17.5}$ 2.2788, $n_D^{17.5}$ 1.54092, $n_D^{17.5}$ 1.54560, and thus contains about 33.5% of the modification, m. p. -6.5°.

The compounds are readily decomposed by alcoholic potassium

hydroxide according to the equation :



the isomeride, m. p. -53° , being by far the more readily decomposable.

H. W.

An Application of Young's Method for the Preparation of Absolute Alcohol. GEORGES CHAVANNE (*Bull. Soc. chim. Belg.*, 1913, 27, 205—209).—The author criticises Young's method of dehydrating aqueous alcohol by means of benzene, and has examined the effect of substituting *s*-dichloroethylene for the latter substance. The general course of the process is similar in each case. *s*-Dichloroethylene, d. p. 48.35° , yields with aqueous alcohol a ternary mixture, b. p. 44.4° , which has the composition, *s*-dichloroethylene 94.5%, alcohol 4.4%, water 1.1%. The binary mixture of *s*-dichloroethylene and alcohol has d. p. 46.5° and contains 94.0% of the former, whilst the binary mixture of *s*-dichloroethylene and water, containing 98.1% of the former, has d. p. 45.3° . With the isomeric *s*-dichloroethylene, b. p. 60.25° , the ternary mixture has the composition, *s*-dichloroethylene 90.5%, alcohol 6.65%, water 2.85%, and b. p. 53.8° . The binary mixture of *s*-dichloroethylene and alcohol, containing 90.2% of the former, has d. p. 57.7° , whilst the corresponding mixture of *s*-dichloroethylene and water contains 96.65% of the former and has b. p. 53.3° . The following are the main conclusions:

(i) The loss of alcohol due to the formation of a ternary mixture is rather greater than when benzene is used if the isomeride, b. p. 48.35° , is employed, rather less in the case of the isomeride, b. p. 60.25° . The use of a mixture of equal weights of the two isomerides, corresponding approximately with commercial *s*-dichloroethylene, leads to a slightly greater loss of alcohol than is the case with benzene, whilst the employment of the equilibrium mixture gives results practically identical with those obtained with the aid of benzene.

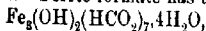
(ii) In practice, a portion of the alcohol would also be removed in the form of a binary mixture. Such loss, however, would be less serious than that encountered when benzene is used, since the binary mixtures of alcohol and *s*-dichloroethylene are poorer in alcohol than the corresponding mixtures of alcohol and benzene.

(iii) The use of the dichloro-derivatives has the advantage that the b. p. of alcohol is 20.6° higher than that of the least volatile binary mixture. In this respect, the dichloro-derivatives are superior to benzene or *n*-hexane.

The author is led to the conclusion that the above method is not suited to the commercial preparation of absolute alcohol, since the losses are much greater than those involved by the use of lime.

H. W.

Composition of Certain Formates. CHARLES H. HAMPSHIRE and W. R. PRATT (*Pharm. J.*, 1913, 91, 138—142).—An examination of commercial specimens of the principal formates and an investigation of the methods of preparation gave the following results: Sodium formate sometimes consists of the anhydrous salt and sometimes of crystals of the dihydrate. Ferric formate has the formula,



assigned to it by Belloni (*A.*, 1909, i, 283), and not $Fe_2(HCO_2)_6 \cdot H_2O$,
3 s 2

as stated in the B. P. Codex. Magnesium formate has the formula $Mg(HCO_2)_2 \cdot 2H_2O$, and calcium formate the formula $Ca(HCO_2)_2$. Quinine formate is not anhydrous, but has the composition $C_{20}H_{24}O_2N_2 \cdot HCO_2H \cdot H_2O$.

When freshly prepared, strychnine formate contains $2H_2O$, but it effloresces quickly.

W. P. S.

Esters of Palmitic Acid. MARJORY STEPHENSON (*Biochem. J.*, 1913, 7, 429—435).—Palmityl chloride, a colourless oil, b. p. 198—200°/15 mm., condenses with glycol in presence of pyridine with chloroform as a solvent to *ethylene dipalmitate*, $(C_{15}H_{31} \cdot CO_2)_2C_2H_4$, which crystallises in rosettes of fine needles, m. p. 65° (corr.).

Glyceryl tripalmitate (tripalmitin), prepared in a similar manner, crystallises in colourless, fine needles, m. p. 62° (corr.).

Mannityl hexapalmitate crystallises in rosettes of fine needles, m. p. 64·5° (corr.).

Dextrose pentapalmitate,

$C_{15}H_{31} \cdot CO_2 \cdot CH_2 \cdot [CH \cdot O \cdot CO \cdot C_{15}H_{31}]_4 \cdot CHO$,
has m. p. 62°.

E. F. A.

The Action of Complex-forming Acids or their Salts on Platinum Ammonia Compounds. II. Reactions with Ethylthiolacetic Acid. LUDWIG RAMBERG (*Ber.*, 1913, 46, 2353—2362. Compare this vol., ii, 607).—An intermediate product of the action of ethylthiolacetic acid on *cis*-dinitritodiammineplatinum is *nitratodiammineplatinum ethylthiolacetate*, $Pt(NH_3)_2(NO_2)(CO_2 \cdot CH_2 \cdot SEt)$, which crystallises in large, colourless prisms, m. p. 188—189°. When distilled with dilute sodium hydroxide only one half of the ammonia is liberated. When, however, ethylthiolacetic acid is added to dissolve the compound and then, after an interval, it is distilled with sodium hydroxide, the whole of the ammonia is set free. When the above nitratodiammineplatinum ethylthiolacetate is boiled with concentrated acetic acid one molecule of ammonia is liberated, and *nitratomonamineplatinum ethylthiolacetate*, $CH_2 \begin{smallmatrix} CO \cdot O \\ \diagdown \end{smallmatrix} P \begin{smallmatrix} NO_2 \\ \diagup \end{smallmatrix} \begin{smallmatrix} NH_3 \\ SEt \end{smallmatrix}$, is obtained. This crystallises in large, flat, colourless prisms, grouped in rosettes, m. p. 193—194° (decomp.).

On shaking *cis*-dinitritodiammineplatinum with an aqueous solution of ethylthiolacetic acid in a closed tube only a little dissolves, and some nitrous fumes are liberated on opening the tube. If, however, sodium ethylthiolacetate is substituted for the free acid and the mixture is boiled in an open vessel, the main product is *sodium dinitritobis(ethylthiolacetato)platinoate*, $(CO_2Na \cdot CH_2 \cdot SEt)_2Pt(NO_2)_2 \cdot 2H_2O$, which is also obtained on adding sodium nitrite to α -platinoethylthiolacetate; it forms small, colourless crystals.

trans-Dichlorodiammineplatinum reacts with ethylthiolacetate to form a colourless, complex substance of the composition

$Pt_2(NH_3)_4Cl_2(CO_2 \cdot CH_2 \cdot SEt)(CO_2H \cdot CH_2 \cdot SEt)$,
which evolves ammonia only slowly when distilled with sodium hydroxide, and decomposes on boiling with acetic acid into *trans*-dichloro-

diammineplatinum, *trans*-diammineplatinum bisethylthiolacetate, and ethylthiolacetic acid. Hence the formula given should probably be doubled.

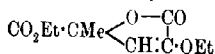
Ethylthiolacetic acid combines with *trans*-dinitratodiammineplatinum to the compound $\text{Pt}(\text{NH}_3)_2(\text{NO}_3)_2 \cdot 2\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{SEt}, \text{H}_2\text{O}$; this crystallises in colourless rosettes of prismatic crystals, m. p. 115–116°.

Ethylthiolacetic acid and *trans*-sulphatodiammineplatinum combine to form the *additive product*, $\text{Pt}(\text{NH}_3)_2\text{SO}_4 \cdot 2\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{SEt}$, which crystallises in colourless tablets or prisms. It reacts with potassium platinochloride, K_2PtCl_6 , forming platinoethylthiolacetate, which reacts with hydrogen chloride, forming *monochloro-(bisethylthiolacetato)-platinic acid*, $(\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{SEt})\text{PtCl}(\text{CO}_2\text{CH}_2 \cdot \text{SEt})$, and *trans*-dichlorodiammineplatinum, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. The former compound crystallises in greenish-yellow aggregates, m. p. 166–167°.

The above sulphate reacts with barium hydroxide, yielding colourless, microscopic needles of *trans*-diammineplatinum bisethylthiolacetate, which can also be obtained from the corresponding iodide on boiling with silver ethylthiolacetate. It has m. p. 200–203° (decomp.).

trans-Dinitritodiammineplatinum and sodium ethylthiolacetate react very slowly, yielding the same sodium dinitrito-(bisethylthiolacetato)-platinato as was derived from the *cis*-derivative. E. F. A.

Lactonisation of α -Ketonic Esters. HENRI GAULT (*Compt rend.*, 1913, 157, 135–137. Compare A., 1911, i, 709).—By a study of its compounds with hydrazine and ammonia the author has definitely established the constitution of the neutral substance, b. p. 176–177°/13 mm., obtained by saturating ethyl pyruvate with hydrogen chloride in the cold, as being the ethyl ether of the enolic form of ethyl α -keto- γ -valerolactone- γ -carboxylate,



compare A., 1912, i, 237). It unites with hydrazine (1 mol.) to form the *lactone hydrazide*, $\text{NH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CMe} \begin{array}{l} \text{O} \\ \text{CO} \\ \text{CH} \cdot \text{C} \cdot \text{OEt} \end{array}$, m. p. 46°, and a small quantity of a crystalline compound, m. p. 230° (decomp.), obtained at the same time. With excess of hydrazine it gives the *pyrazinolactone hydrazide*, $\text{NH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CMe} \begin{array}{l} \text{O} \\ \text{C}(\text{OH}) \cdot \text{NH} \cdot \text{NH}_2 \\ \text{CH} \cdot \text{C} \cdot \text{OEt} \end{array}$, m. p. 186° (decomp.).

Ammonia reacts similarly in the cold, giving an *amide*, m. p. 190°, and a second compound, m. p. 245° (decomp.). The compound, m. p. 230°, obtained in the action with hydrazine (1 mol.) and the compound, m. p. 245°, obtained in the action with ammonia are shown to be derivatives of ethyl α -chloro- γ -keto- α -methyl-utarate, formed during the aldolisation of the pyruvic ester.

W. G.

Catalytic Preparation of Ketones Over Oxides of Iron. ALPHONSE MAILHE (*Compt. rend.*, 1913, 157, 219—221).—Both ferrous and ferric oxides can replace cadmium oxide (compare this vol., i, 828) as catalysts in the preparation of simple or mixed ketones from their acids. The oxides are kept at a temperature of 430—490°. The acids employed may be aliphatic or aromatic, or mixtures of the two, and, as in the case of cadmium oxide, *isovaleric* and *isobutyric* acids give the worst yields. The yields are given for numerous ketones.

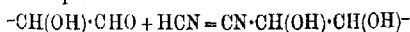
W. G.

The Mechanism of the Formation of Acrose. ERNST SCHMITZ (*Ber.*, 1913, 46, 2327—2335).—At the time of their identification of α -acrose as *dl*-fructose, Fischer and Tafel suggested that the accompanying β -acrose present in smaller amount in the product from dibromopropaldehyde and from glycerose was a sugar probably allied to sorbose. From the occurrence of a ketose it is obvious that the process cannot be a simple aldol condensation of glyceraldehyde, but that at some stage of the change an aldehyde group must become transformed into a ketonic one; this probably occurs in the triose molecule, as the conditions of the condensation are not such as to cause a rearrangement in the hexose molecule; it has also been shown (Wohl and Neuberg, A., 1901, i, 12) that the trioses are easily interconvertible under these conditions, because whether aldehyde-free glycerose or pure glyceraldehyde is applied for the condensation, β -acrose is always produced.

By the condensation of pure glyceraldehyde, obtained conveniently by the hydrolysis of the corresponding acetal with *N*/10-sulphuric acid and subsequent treatment with baryta, under the influence of 0.1% excess of baryta at the ordinary temperature, a solution was obtained which yielded a crystalline mixture of two hexoses; this could be separated by recrystallisation from hot methyl alcohol; the less soluble constituent, needles, m. p. 129—130°, D^{16} 1.665, osazone n. p. 216—217°, was *dl*-fructose, whilst the more soluble, rhombic leaflets, m. p. 162—163°, D^{17} 1.634, osazone m. p. 169—170° (decomp.), was *dl*-sorbose, the identity being confirmed by comparison with an artificial mixture of the enantiomorphous forms. The *dl*-fructose, here obtained crystalline for the first time, of course represents α -acrose, whilst the *dl*-sorbose in spite of the somewhat higher m. p. doubtless represents the β -acrose which had previously not been obtained in a quite pure condition. The formation of a racemic sorbose would be expected on theoretical grounds from the condensation of dihydroxyacetone with *dl*-glyceraldehyde.

D. F. T.

Cyanohydrins of Certain Monosaccharides. CYRILL KRAUZ and JAN KLOUD (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 397—401).—On the addition of hydrogen cyanide to a monosaccharide, two epimeric cyanohydrins are produced:



(compare Votoček, A., 1911, i, 179). A study has now been made of

the products obtained by the action of hydrogen cyanide on certain monosaccharides.

When arabinose is treated with solution of hydrogen cyanide, a mixture of the amides of 1-gluconic and 1-mannonic acids is obtained; the former has m. p. 181° , not 160° (decomp.) as stated by Kiliani (A., 1887, 230). In the case of xylose and rhamnose, liquid products were obtained which could not be separated. Rhodose yields α - and β -rhodohexonamides (Kraus, A., 1910, i, 224). Fucose furnishes α -fucohexonamide and β -fucohexonamide, m. p. 176° . With galactose, α -galactohexonamide, m. p. 201° , was obtained; the mother liquor when treated with phenylhydrazine gave the phenylhydrazone of this amide, m. p. 226° , together with another phenylhydrazone, m. p. 186° . Mannose yields a mixture of α - and β -mannohexonamides, the former melting at 214 – 215° , and not at 182 – 183° (Fischer and Hirschberger, A., 1889, 482).
E. G.

Hydrolysis of Cellulose. I. RICHARD WILLSTÄTTER and LÁSZLÓ ZECHMEISTER (*Ber.*, 1913, 46, 2401–2412).—Whereas ordinary concentrated hydrochloric acid (37.6% of hydrogen chloride) decomposes and gelatinises cellulose after about a day's action, a more concentrated acid (40–41% of hydrogen chloride) dissolves cellulose completely within a few seconds. At first the cellulose can be precipitated again, but it is rapidly hydrolysed, and finally only dextrose remains in solution. It is possible to follow the course of the change both polarimetrically and gravimetrically, whereby 96% of the theoretical quantity of dextrose is obtained. The 1% solution of cellulose in the concentrated acid is at first optically inactive; it becomes active after about an hour, and increases until hydrolysis is complete in twenty-four to forty-eight hours at the ordinary temperature. The change in rotatory power gives indication of the intermediate formation of higher carbohydrates. An acid, D¹⁵ 1.212 (41.4% of hydrogen chloride), dissolves 15% of cellulose; the solution is at first colourless and clear; in time it becomes yellow, and later dark yellow as the dextrose is decomposed. On dilution of the solution during the first half-hour, unchanged cellulose is precipitated.

Cellulose dissolves similarly in 66% (D 1.78) hydrogen bromide, but not in concentrated hydriodic acid; hydrofluoric acid (70–75% of hydrogen fluoride) gelatinises, and quickly dissolves cellulose.

Pine-wood dissolves quickly in fuming hydrochloric acid, leaving 30% of its weight undissolved as lignin substance.

The rotatory power of dextrose ($[\alpha]_D$) increases from $+54.5^{\circ}$ in hydrochloric acid D 1.018 to $+97.5^{\circ}$ in an acid D 1.204, $+106^{\circ}$ in an acid D 1.212, and $+164.6^{\circ}$ in a 44.5% acid.
E. F. A.

Certain Substances containing the Cetyl Radicle. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1913, 27, 217–225).—Triethylammonium iodide, $C_{16}H_{33}\cdot NEt_3I$, is obtained when a mixture of triethylamine and cetyl iodide is heated for two hours at 130° . It dissolves in water, yielding soapy solutions, which develop an abundant

lather when shaken. These solutions only give an opalescence with silver nitrate, and thus appear to be colloidal, this observation being confirmed by a study of their b. p.'s and electrical conductivities. The solid iodide has m. p. $179-181^{\circ}$ without decomposition (contrast Kraft and Moye, A., 1889, 689).

An attempt has been made to prepare triethylcetylammmonium hydroxide by the action of freshly prepared silver oxide on a boiling alcoholic solution of the corresponding iodide. Under these conditions, however, the base, if formed, is decomposed into diethylcetylamine.

Aqueous solutions of diethylcetylamine hydrochloride behave similarly to those of the above iodide. Determinations of the conductivity at different temperatures show that a period of rapid crystallisation occurs in the region of 0° . The values obtained for the molecular conductivity are greater than those observed for triethylcetylammmonium iodide at similar dilutions.

Triethylcetylammmonium cetyl-sulphonate, $C_{16}H_{33}\cdot SO_3\cdot NEt_3\cdot C_{16}H_{33}$, is readily prepared by heating a boiling alcoholic solution of *silver cetyl-sulphonate* with triethylcetylammmonium iodide. It is molten at $172-179^{\circ}$ without showing any distinct m. p. It yields soapy solutions in hot water, which, on cooling, separate into a clear liquid and a jelly-like mass. It is soluble in alcohol and in ethyl acetate. From the latter it separates in crystals, m. p. about 53° , which contain solvent of crystallisation. Determinations of the conductivity of aqueous solutions lead to the conclusion that the substance is probably present in the form of multi-molecular aggregates.

In chemical constitution and in the behaviour of their aqueous solutions or pseudo-solutions, these substances are somewhat analogous to soaps. This is confirmed by the fact that solutions of triethylcetylammmonium iodide or, better, of diethylcetylamine hydrochloride in water yield excellent results in the cleansing of samples of wool.

H. W.

The Homologue of Muscarine in the C_3 Series V. BRABANT (*Zeitsch. physiol. Chem.*, 1913, 86, 206-214).—To prepare β -homomuscarine acetaldehyde is converted into ethyl α -dichloropropyl ether, $CH_2Cl\cdot CH_2\cdot CHCl\cdot OEt$, and this into the ethylacetal of β -chloropropaldehyde, $CH_2Cl\cdot CH_2\cdot CH(OEt)_2$. When this is heated with trimethylamine in a sealed tube on the water-bath, the hydrochloride of β -homomuscarineacetal, $NMe_3Cl\cdot CH_2\cdot CH_2\cdot CH(OEt)_2$, is obtained.

This is hydrolysed by concentrated hydrochloric acid to β -homomuscarine hydrochloride, $NMe_3Cl\cdot CH_2\cdot CH_2\cdot CHO$, which shows all the typical reactions of both aldehyde and amino-groups.

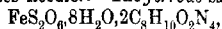
β -Homomuscarineacetal hydrochloride forms stellate aggregates of small needles which are very hygroscopic; the *platinichloride* forms large, prismatic-rhombic, orange-red crystals which blacken at 160° , m. p. $190-195^{\circ}$ (decomp.); the *aurichloride* separates in broad, lustrous, straw-yellow needles, m. p. $93-95^{\circ}$ (decomp.).

β -Homomuscarine hydrochloride forms hygroscopic crystals; the free base could not be isolated. The *platinichloride* separates in microscopic, orange-yellow rods, decomp. $156-160^{\circ}$. The *auri-*

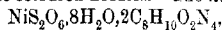
chloride is straw-yellow, m. p. 150—155° (decomp.). The semicarbazone crystallises in small, colourless, regular octahedra, m. p. 247.5° (corr.).

E. F. A.

Compounds of Hydrated Salts with Organic Bases (Dithionates, Sulphates, Thiosulphates). FILIPPO CALZOLARI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 787—792. Compare A., 1912, i, 812).—The dithionate, $\text{MgS}_2\text{O}_6 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{10}\text{O}_2\text{N}_4$, prepared from magnesium dithionate and a large excess of caffeine, forms colourless, prismatic crystals. The manganese derivative, $\text{MnS}_2\text{O}_6 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{10}\text{O}_2\text{N}_4$, crystallises in colourless needles. The ferrous salt,



forms prismatic crystals. The cobalt salt, $\text{CoS}_2\text{O}_6 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{10}\text{O}_2\text{N}_4$, crystallises in pale rose-coloured needles. The nickel salt,

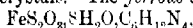


forms green crystals isomorphous with those of the cobalt compound.

The compound of magnesium dithionate with hexamethylenetetramine, $\text{MgS}_2\text{O}_6 \cdot 6\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$, forms large crystals. The manganese compound, $\text{MnS}_2\text{O}_6 \cdot 6\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$, is a white, crystalline powder. The ferrous salt, $\text{FeS}_2\text{O}_6 \cdot 6\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$, is a greenish-white, crystalline powder. The cobalt salt, $\text{CoS}_2\text{O}_6 \cdot 6\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$, forms rose-red, regular crystals. The nickel salt, $\text{NiS}_2\text{O}_6 \cdot 6\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$, forms green crystals similar to those of the cobalt compound.

The compound of magnesium sulphate and hexamethylenetetramine, $\text{MgSO}_4 \cdot 9\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$, forms colourless crystals. The manganese compound, $\text{MnSO}_4 \cdot 9\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$, forms colourless crystals, and mixed crystals of this compound with that of nickel were also obtained. The ferrous compound, $\text{FeSO}_4 \cdot 9\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$, must be prepared in the absence of air. The cobalt compound, $\text{CoSO}_4 \cdot 9\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$, forms rose-red crystals, and mixed crystals of it with the magnesium compound can be obtained. The nickel compound, $\text{NiSO}_4 \cdot 9\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$, forms large, emerald-green crystals isomorphous with those of the cobalt salt.

The compound of magnesium thiosulphate with hexamethylenetetramine, $\text{MgS}_2\text{O}_3 \cdot 8\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$, forms colourless, rhombohedral crystals. The manganese compound, $\text{MnS}_2\text{O}_3 \cdot 8\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$, forms very pale rose-coloured crystals. The ferrous compound,



must be prepared out of contact with the air; it forms greenish-white crystals. The cobalt salt, $\text{CoS}_2\text{O}_3 \cdot 8\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$, forms rose-coloured crystals. The nickel compound, $\text{NiS}_2\text{O}_3 \cdot 8\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$, forms emerald-green crystals.

R. V. S.

Condensation of Amino-acids with Formaldehyde. GIRO GALEOTTI (*Biochem. Zeitsch.*, 1913, 53, 474—492).—On heating amino-acids with formaldehyde, products are obtained which differ both from the original acids and fresh mixtures of the reacting products. Reddish-yellow solutions are obtained, which do not deposit crystals, but yield an amorphous residue on evaporating off the water. The solutions are acid, and only the tyrosine derivative is precipitated on the addition of dilute acids. The glycine, alanine, aspartic acid

and tyrosine derivatives are insoluble in alcohol or acetone, but the leucine and phenylalanine derivatives are soluble. All are insoluble in ether. The aqueous solutions give voluminous precipitates with phosphotungstic, picric and tannic acids, and with the salts of heavy metals. They do not reduce copper salts in alkaline solution, give the diazo-reaction with a yellowish-red or cherry-red colour, and give precipitates on saturation with ammonium sulphate. They dissolve copper hydroxide, yielding malachite-green solutions which give a precipitate on addition of alcohol. They no longer contain the amino-group, as no nitrogen is evolved in the van Slyke reaction, which can be employed for tracing the course of the reaction of the aldehyde on the acids. The glycine derivative was studied in some detail. It has a molecular weight of 288, corresponding with the formula $C_{12}H_{21}O_5N_3$, and m. p. 164° . Attention is called to the similarity in the behaviour of the compounds obtained to the polypeptides, and it is suggested that formaldehyde may play some part in forming complex derivatives from amino-acids in living organisms, analogous to the supposed formation of carbohydrates by condensation with this substance.

S. B. S.

Synthesis of the Anhydrides of α -Aminoacyl Glucosamines. CHARLES WEIZMANN and ARTHUR HOPWOOD (*Proc. Roy. Soc.*, 1913, A, 88, 455—461. Compare P., 1912, 28, 261).— α -Bromoacyl haloids are condensed with glucosamine hydrochloride in the presence of sodium hydroxide (compare P., 1912, 28, 261), and cold aqueous ammonia is allowed to act on the α -bromoacylglucosamines formed. Anhydrides of the expected α -aminoacylglucosamines are obtained.

Alanineglucosamine anhydride separates in colourless, prismatic needles, which turn brown at 245 — 250° , and melt at 269 — 272° to a black liquid. It reduces Fehling's solution on prolonged boiling, but does not react with either phenylhydrazine or semicarbazide.

Leucylglucosamine anhydride forms similar colourless, prismatic needles, which sinters at 205° , m. p. 213 — 215° (decomp.).

α -Aminolaurylglucosamine anhydride was obtained in colourless crystals.

E. F. A.

Esters of Imino- and Oximino-carbonic Acid. JOSEPH HÖUBER and ERICH SCHMIDT (*Ber.*, 1913, 46, 2447—2460).—Sandmeyer (A., 1886, 611) claimed to have reduced esters of chloroiminocarbonic acid, and obtained ethyl iminocarbonate, $HN:C(OEt)_2$, which was dried over potassium hydroxide. It is shown that under these conditions urethane is formed, and that it was present in Sandmeyer's product.

When the reduction product is carefully dried over ignited sodium sulphate and fractionated in a vacuum, pure iminocarbonic esters are obtainable. Even the pure esters change on prolonged keeping into crystalline cyanuric acid derivatives.

The hydrochloride of the imino-ester is to be regarded as a chloro-imino-ether, $NH_2 \cdot CCl(OR)_2$. In presence of water the chlorine is exchanged for hydroxyl, $NH_2 \cdot C(OR)_2 \cdot OH$, HCl, following which the hydrogen chloride conditions elimination of ammonium chloride and the formation of alkyl carbonate, $CO(OR)_2$.

Similarly, with hydroxylamine the compound
 $\text{NH}_2\cdot\text{C}(\text{OR})_2\cdot\text{NH}\cdot\text{OH}\cdot\text{HCl}$

formed decomposes into the oximinocarbonic ester, $\text{C}(\text{OR})_2\cdot\text{N}\cdot\text{OH}$. Working in ethereal solution it was possible to prepare *diethyl* or *dimethyl oximinocarbonate* in this manner, and the method has been extended to the preparation of the true hydroximic esters of the aliphatic series, $\text{OEt}\cdot\text{CR}\cdot\text{N}\cdot\text{OH}$.

The oximinocarbonic esters, which crystallise well, are obtained by a similar process from the chloroiminocarbonic esters.

Ethyl chloroiminocarbonate has m. p. 39° , agreeing with Sandmeyer's statement; during its preparation a product of unknown constitution crystallising in needles, m. p. $148-149^\circ$, is formed.

Methyl chloroiminocarbonate has m. p. 20° , b. p. $63-64/13\text{ mm.}$, without decomposition.

Ethyl iminocarbonate is a transparent liquid of a strongly basic odour, $D_{20}^{25} 0.9637$.

Ethyl iodoiminocarbonate, $\text{NI}\cdot\text{C}(\text{OEt})_2$, forms yellow crystals and crusts. When shaken with mercury in ethereal or alcoholic solution, *acetyl carbonic* carbonate, $\text{C}(\text{OEt})_2\cdot\text{N}\cdot\text{N}\cdot\text{C}(\text{OEt})_2$, is formed.

Ethyl carbamylinoiminocarbonate, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{N}\cdot\text{C}(\text{OEt})_2$, forms crystals sintering at 100° , m. p. 101° .

Ethyl thiocarbamylinoiminocarbonate has m. p. $117-118^\circ$.

E. F. A.

The Organic Acid Amides and their Metallic Derivatives as Acids and Salts of the Ammonia System of Acids, Bases, and Salts. EDWARD C. FRANKLIN (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 119-130. Compare A., 1912, ii, 451).—A recapitulation of the author's classification of amides and their derivatives into "ammono-acids," "ammono-bases," "ammono-salts," "ammono-esters," "mixed ammono-acids," and "acid anammonoides." The ammono-acids vary in strength from acetamide, benzamide, and carbamide, which only form salts in liquid ammonia solution and have only a feeble conductivity in that solvent, to such compounds as phthalimide and "saccharin" which are not excelled in strength by the strongest carboxylic acids.

J. C. W.

Compounds of Ferricarbamide. GIUSEPPE A. BARBIERI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 867-870).—These compounds exhibit complete chemical and crystallographic similarity to the salts of chromicarbamide already known. They are all greenish-blue in the solid state and in concentrated solution, but dilute solutions are yellow and are precipitated by ammonia even in the cold. Compounds analogous to the hydrate and carbonate of chromicarbamide cannot be prepared.

The *perchlorate*, $[\text{Fe}(\text{CON}_2\text{H}_4)_6](\text{ClO}_4)_3$, is obtained by adding a concentrated solution of carbamide to a solution of ferric perchlorate containing excess of perchloric acid, or from a perchlorate and another ferricarbamide compound. It forms mixed crystals with the corresponding *chromicarbamide perchlorate*, $[\text{Cr}(\text{CON}_2\text{H}_4)_6](\text{ClO}_4)_3$, which is a green, crystalline powder.

Ferriccarbamide nitrate, $[\text{Fe}(\text{CON}_2\text{H}_4)_6](\text{NO}_3)_3$, the *permanganate*, $[\text{Fe}(\text{CON}_2\text{H}_4)_6](\text{MnO}_4)_2$, the *dichromate*, $[\text{Fe}(\text{CON}_2\text{H}_4)_6](\text{Cr}_2\text{O}_7)_2$, the *chloride*, $[\text{Fe}(\text{CON}_2\text{H}_4)_6]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$, the *bromide*, $[\text{Fe}(\text{CON}_2\text{H}_4)_6]\text{Br}_3 \cdot 3\text{H}_2\text{O}$, and the *nitrate periodide*, $[\text{Fe}(\text{CON}_2\text{H}_4)_6](\text{NO}_3)_2\text{I}_2$, are similarly prepared. On treating the bromide with bromine an unstable perbromide is obtained.

R. V. S.

Preparation of Melamine and Ammeline from Dicyanodiamide; Triaminomelamine and Diaminoammelne. ROBERT STOLLÉ and K. KRAUCH (*Ber.*, 1913, 46, 2337—2339).—When powdered dicyanodiamide is treated with concentrated ammonia solution in a sealed tube at 120° for three hours, a crystalline deposit is obtained consisting of melamine in 35% yield and of ammeline in 20% yield, which can be separated by the sparing solubility of the latter in water; a small quantity of carbamide and guanidine can be found in the liquid from which the crystalline mass has separated. It is suggested that possibly the dicyanodiamide is acted on concurrently by the ammonia and by water, with the production of guanidine and cyanamide and of guanidine and cyanic acid respectively; unchanged dicyanodiamide then reacts with the cyanamide yielding melamine, and with the cyanic acid yielding ammeline.

Triaminomelamine (cyanuric hydrazide; von Meyer and Nabe, A., 1911, i, 122; Finger, A., 1907, i, 298), microscopic needles, m. p. 287° , was obtained by heating melamine with a quibquemolecular proportion of hydrazine hydrate for five hours under pressure at 150° ; it quickly reduces warm ammoniacal silver nitrate, and when shaken in hydrochloric acid solution with benzaldehyde yields a *tribenzylidene* derivative.

When ammeline is heated with an equal quantity of hydrazine hydrate for five hours under pressure at 130° , diaminoammelne, prisms, m. p. above 340° , is obtained; this in aqueous solution reacts with benzaldehyde, producing a *dibenzylidene* derivative, m. p. 315° .

D. F. T.

Condensation of Melamine with Dextrose. LEOPOLD RADLBERGER (*Chem. Zentr.*, 1913, i, 2110; from *Österr.-ung. Zeitsch. Zuckerind.*, 1913, 42, 236—239).—Melamine and dextrose were condensed by heating in 30% alcoholic solution on the water-bath. The product consisted of 2 mols. melamine to 1 mol. dextrose, namely, $[\text{C}_3\text{N}_3(\text{NH}_2)_2 \cdot \text{NH}]_2 \cdot \text{CH} \cdot [\text{CH} \cdot \text{OH}]_4 \cdot \text{CH}_2 \cdot \text{OH}$. It has m. p. 281° , forming colourless, lustrous crystals which do not reduce Fehling's solution.

E. F. A.

Syntheses of Mercury Fulminate from Propyl Alcohol. A. L. KIBLER (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 239—243).—Experiments are described in which propyl alcohol, isobutyl alcohol, amyl alcohol, acetone, and propaldehyde were substituted for ethyl alcohol in the usual process for the preparation of mercury fulminate. A small quantity of mercury fulminate was obtained from the propyl alcohol, but not from any of the other substances. In the experi-

ments with propyl alcohol, an intermediate compound was isolated, which forms large, white, lustrous plates, and decomposes either spontaneously or when treated with water, leaving traces of a grey powder, probably composed of mercury. E. G.

Azides of Carbamic Acid from Ketens. VII. E. OLIVERI-MANDALÀ and E. CALDERARO (*Gazzetta*, 1913, 43, i, 538—543. Compare this vol., i, 716).—Azoimide reacts with ketens giving azides of carbamic acid. The stages in the reaction are probably indicated by the scheme: $\text{CR}_2\text{CO} \rightarrow \text{CHR}_2\text{CO}\cdot\text{N}_3 \rightarrow [\text{CHR}_2\text{CO}\cdot\text{N}] \rightarrow \text{CHR}_2\text{N}\cdot\text{CO}$, and from this carbimide the azide, $\text{CHR}_2\text{NH}\cdot\text{CO}\cdot\text{N}_3$, is produced by the addition of a further molecule of azoimide.

Keten reacts with an ethereal solution of azoimide at the temperature of a mixture of ice and salt, yielding *methylcarbamazide*, $\text{N}_3\cdot\text{CO}\cdot\text{NHMe}$, which forms lustrous laminae or tablets, m. p. 46—47°. The formation of the azide shows that keten has reacted as though it had the ketonic formula of Staudinger, and not the hydroxylic formula of Wilsmore. With aniline, the azide yields *s*-phenylmethylcarbamide and aniline azoimide. Alcoholic ammonia reacts with the azide, yielding methylcarbamide and ammonium azoimide. Boiling water decomposes the azide, carbon dioxide, azoimide and methylamine being formed; by keeping an aqueous solution of the azide in a desiccator, *methylammonium azoimide*, CH_5N_3 , can be obtained; it is a deliquescent substance, which is completely fused at 115°.

Diphenylketen and azoimide yield *diphenylmethylcarbamazide*, $\text{N}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPh}_2$,

which crystallises in colourless, silky needles, m. p. 121—123°. When heated for four hours at 100—110° in a sealed tube with alcoholic ammonia, the azoimide yields *as*-diphenylmethylcarbamide. When heated with aniline in a sealed tube for two hours at 90°, the azide is converted into *diphenylmethylphenylcarbamide*,

$\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPh}_2$,

which forms silky crystals, m. p. 208—209°. This substance dissolves in concentrated sulphuric acid, giving an orange-red coloration.

R. V. S.

Action of Magnesium Methyl Iodide on Silicon Hexachloride. GEOFFREY MARTIN (*Ber.*, 1913, 46, 2442—2447. Compare P., 1913, 29, 190).—The yellow substance formed by the action of magnesium methyl iodide on silicon hexachloride has the composition $\text{Si}_6\text{H}_6\text{O}_{15}\text{Me}$. When heated, hydrogen and methane are evolved, and a silicon compound is obtained practically without carbon, but which still contains coupled silicon groups, since on dissolution in potassium hydroxide hydrogen is evolved. On the addition of excess of acid, silicic acid is precipitated. E. F. A.

Researches on the Direct Introduction of Substituents into the Benzene Nucleus During the Years 1910, 1911, and 1912. ARNOLD F. HOLLEMAN (*Chem. Weekblad*, 1913, 10, 604—620).—A summary of papers on this subject published since the issue of

the author's work, "Die direkte Einführung von Substituenten in den Benzolkern," in the year 1910. A. J. W.

A Simple Method of Preparing Hexamethylbenzene. HANS RECKLEBEN and JOHANNES SCHEIBER [with K. SCHNABEL] (*Ber.*, 1913, 46, 2363—2365).—When the vapour from a molecular mixture of acetone and methyl alcohol is passed over aluminium oxide, heated at about 400°, clean crystals of hexamethylbenzene are obtained in about 10% of the theoretical quantity. The oily residue represents a complicated mixture. Replacement of aluminium oxide by other oxides led to unfavourable results.

On bromination of hexamethylbenzene, a mixture of bromides, m. p. 231—269°, and containing from 64% to 80% of bromine, is obtained. E. F. A.

Nitro-derivatives of High-boiling Mineral Oils. KONSTANTIN CHARITSCHKOFF (*Chem. Zeit.*, 1913, 37, 869).—When Caucasian lubricating oils are warmed with fuming nitric acid, they form syrupy, very viscous nitro-derivatives, which are soluble in most organic solvents with the exception of light petroleum. They are weak acids, dissolve in alkalis, and form insoluble salts with the alkaline earths and heavy metals which are similar to the salts of polynaphthene acids (*A.*, 1910, i, 110). Moreover, their composition and properties agree with those of the nitro-derivatives of polynaphthene acids.

J. C. W.

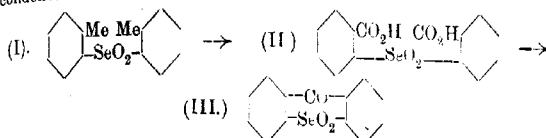
The Reaction Between Selenic Acid and Toluene. HOWARD WATERS DOUGHTY and FRANK ROSE ELDER (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 93—101).—Toluene and concentrated selenic acid were left together for some months during which time carbon dioxide was evolved. The lower, dark red, viscous layer was then poured into water and separated into an acid solution and a small amount of a red oil with a solid admixture.

The acid solution was exactly neutralised with barium hydroxide, filtered from barium selenate, evaporated to dryness, and extracted during several days with chloroform, which removed traces of the above red oil. The residue gave a mixture of *o*- and *p*-tolueneselenonic acids which could not be separated, but on reduction of a concentrated solution with hydrogen chloride, *p*(*l*)-tolueneseleninic acid, $C_6H_4Me \cdot SeO_3H \cdot H_2O$, was precipitated in long, silky, white needles, m. p. 160°, whilst the mother liquor yielded *o*(*l*)-tolueneseleninic acid, with $\frac{1}{2}H_2O$, in nodules of short, white needles, m. p. 99—101°.

The red oil was washed with ether in which the solid substance is insoluble, and then distilled. It had b. p. 201—202°/18—20 mm., and solidified to a light yellow, crystalline mass, m. p. 69·5—70·5°, which was identified with *p*-ditolyl selenide (Zeiser, *A.*, 1895, i, 512). On oxidation with hot permanganate, it yielded diphenylselenone-4:4'-dicarboxylic acid, $SeO_3(C_6H_4 \cdot CO_2H)_2$, as a heavy, white solid, m. p. 283°, which is sparingly soluble in hot alcohol, and insoluble in all other common solvents.

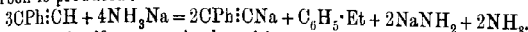
The crystalline substance, insoluble in ether or water, was recrystal-

lised from alcohol in colourless, stout, hexagonal prisms, m. p. 183°. It was not affected by boiling alkalis or permanganate, but yielded salicylic acid on fusion with potassium hydroxide. It is, therefore, *benzophenoneselenone* (III), and its formation is explained by assuming that *o*-ditolyl selenide (I) is formed as an intermediate product, and is then oxidised to diphenylselenone-2:2'-dicarboxylic acid (II), which condenses with loss of carbon dioxide and water.



J. C. W.

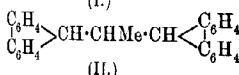
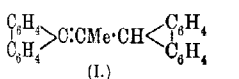
Action of Sodium in Liquid Ammonia on Phenylacetylene and Styrene. PAUL LEBEAU and MARIUS PICON (*Compt. rend.*, 1913, 157, 223—224. Compare this vol., i, 950).—Sodium in liquid ammonia reacts with phenylacetylene, giving the corresponding sodium derivative (2 mols.) and ethylbenzene (1 mol.), with the formation of sodamide. Unlike the true acetylenes of the fatty series, the hydrogenation does not stop at the ethylenic hydrocarbon, but the fully saturated hydrocarbon is produced:



Styrene itself reacts slowly with sodium in liquid ammonia, the products being ethylbenzene and sodamide.

W. G.

A Yellow Hydrocarbon of the Fluorene Series. RUDOLF PUMMERER and GUSTAV DORFMÜLLER (*Ber.*, 1913, 46, 2386—2389).—When fluorene is heated with lead dioxide and sodium ethoxide in pyridine solution, small quantities of a yellow hydrocarbon are formed, owing to the formation of acetaldehyde, and coupling of this with two molecules of fluorene. The final product is *dehydroethylidenefluorene* (I), but *ethylidenefluorene* (II) is formed first, and may also be obtained by reducing the dehydro-compound with zinc dust and acetic acid.



It is very readily oxidised by lead dioxide and even by atmospheric oxygen. The double bond only very slowly absorbs bromine, and does not react with permanganate in pyridine solution.

Dehydroethylidenefluorene crystallises in oblique-ended, yellow prisms; it darkens at 280°, but has not melted at 350°. In small quantities it apparently distils unchanged.

Ethylidenefluorene is colourless, m. p. 262—263°, to a yellowish-brown liquid.

E. F. A.

Orthohalogenated *p*-Nitroanilines and their Derivatives. WILHELM KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 823—836).—2-Chloro-4-nitroaniline forms pale yellow

needles, m. p. 104.5°. Its acetyl derivative crystallises in straw-coloured prisms, m. p. 139°.

3-Chloro-4-bromo-1-nitrobenzene (obtained from the perbromide of the diazonium compound of the preceding substance) forms colourless needles or prisms, m. p. 62°.

3-Chloro-4-iodo-1-nitrobenzene (similarly prepared) crystallises in almost colourless needles, m. p. 103°.

2-Bromo-4-nitroaniline crystallises in pale yellow needles, m. p. 104.5°. Its monoacetyl derivative forms flat prisms, m. p. 114°; the diacetyl derivative in stout prisms, m. p. 132°.

From the amino-derivative by diazotisation, 4-chloro-3-bromo-1-nitrobenzene can be obtained; it crystallises in almost colourless prisms, m. p. 61°, and is identical with the compound obtained from 6-chloro-3-nitroaniline. The corresponding 3-bromo-4-iodo-1-nitrobenzene crystallises in needles or prisms, m. p. 106°. 2-Iodo-4-nitroaniline, m. p. 109°, occurs in yellowish-red prisms and also in golden-yellow laminae; the former is the more stable form. The substance yields a monoacetyl and a diacetyl derivative.

2-Iodo-4-nitroaniline can be diazotised, and by the subsequent introduction of chlorine, 4-chloro-3-iodo-1-nitrobenzene can be prepared; it crystallises in colourless needles, m. p. 78°, and is identical with the compound obtained from 6-chloro-3-nitroaniline in a similar way.

2:6-Dichloro-4-nitroaniline crystallises in lemon-yellow needles, m. p. 195°. It is best diazotised in nitric acid (D 1.38) at 0°. It yields a monoacetyl derivative (almost colourless, flat needles, m. p. 215°) and a diacetyl derivative, m. p. 142.5°, which crystallises in prisms of the monoclinic system

[E. Artini: $a:b:c = 1.1361:1.08753$; $\beta = 70.4^\circ$, D 1.565].

When an alcoholic solution of the preceding amino-compound containing a little concentrated sulphuric acid is treated with ethyl nitrite, 3:5-dichloro-1-nitrobenzene is produced; it crystallises in colourless plates, m. p. 65.4°. On reduction with tin and hydrochloric acid it yields the corresponding dichloroaniline, which forms needles or prisms, m. p. 51.5°. From this substance, 1:3:5-trichlorobenzene is obtainable; it crystallises in colourless needles, m. p. 63.3°, and is identical with that obtained from 2:4:6-trichloroaniline, m. p. 77.5°. 3:5-Dichloro-1-bromobenzene crystallises in colourless needles, m. p. 75.8°. 3:5-Dichloro-1-iodobenzene has m. p. 54°; it is identical with that obtained from 2:4-dichloro-6-iodoaniline, m. p. 84°.

3:4:5-Trichloro-1-nitrobenzene (from 2:6-dichloro-4-nitroaniline) forms pale yellow prisms, m. p. 72.5°. On reduction and elimination of the amino-groups it yields 1:2:3-trichlorobenzene, m. p. 50.8°, identical with that obtained from 2:6-dichloroaniline (Körner and Contardi, A., 1909, i, 220).

3:5-Dichloro-4-bromo-1-nitrobenzene (from the dichloronitro-derivative) crystallises in pale yellow prisms, m. p. 88°.

3:5-Dichloro-4-iodo-1-nitrobenzene forms yellow prisms, m. p. 154.8°. On reduction with ferrous sulphate and ammonia, and subsequent elimination of the amino-group, it yields 1:3-dichloro-2-iodobenzene, which crystallises in thin, colourless plates, m. p. 68°. The same

substance can be prepared from the 2:6-dichloroaniline already mentioned.

2:6-Dibromo-4-nitroaniline (by the action of bromine on *p*-nitroaniline) crystallises in golden-yellow laminae, m. p. 202.5°. Its monoacetyl derivative forms almost colourless needles, m. p. 232°. The diacetyl derivative, m. p. 136°, crystallises in the pinacoid class of the triclinic system [$a:b:c=1.0901:1:0.8325$, $\alpha\ 88^\circ43'4''$, $\beta\ 70^\circ49'34''$, $\gamma\ 93^\circ25'39''$, D 1.939].

3:5-Dibromo-1-nitrobenzene is obtained by diazotising (in alcoholic solution containing sulphuric acid) either 2:6-dibromo-4-nitroaniline or 4:6-dibromo-2-nitroaniline; it crystallises in thin, almost colourless laminae, m. p. 104.5°. From it *s*-chlorodibromobenzene (m. p. 119°) and *s*-dibromiodobenzene (m. p. 124.8°) can be readily prepared. These substances can also be obtained from the following corresponding halogenated anilines: 4-chloro-2:6-dibromoaniline (m. p. 102°); 2:6-dibromo-4-iodoaniline (colourless needles, m. p. 147°); 2:4-dibromo-6-iodoaniline (colourless needles, m. p. 123.5°).

3:4:5-Tribromo-1-nitrobenzene (from the perbromide of the diazo-compound of the dibromonitroaniline already mentioned) crystallises in yellow prisms, m. p. 111.9°. On diazotisation and elimination of the amino-group it yields 1:2:3-tribromobenzene, m. p. 87.8°.

4-Chloro-3:5-dibromo-1-nitrobenzene (obtained in an analogous manner to the nitrotribromo-derivative) crystallises in yellow, tabular prisms, m. p. 92.7°. On reduction and elimination of the amino-group it yields 1-chloro-2:6-dibromobenzene, which forms colourless plates, m. p. 71°, and is identical with the product obtained from the corresponding dibromoaniline.

3:5-Dibromo-4-iodo-1-nitrobenzene crystallises in prisms, m. p. 135.5°. It is not possible to reduce this compound without altering it. The corresponding 1:3-dibromo-2-iodobenzene (colourless, tabular prisms, m. p. 72°) is prepared from *o*-dibromoaniline.

2:6-Di-iodo-4-nitroaniline (from iodine chloride and an acetic acid solution of *p*-nitroaniline) forms golden-yellow scales or flat needles, m. p. 245°. Its monoacetyl derivative forms slightly yellow needles, m. p. 249°; the diacetyl derivative forms stout prisms, m. p. 171°, of the pinacoid class of the triclinic system [$a:b:c=0.9682:0:0.7260$, $\alpha\ 83^\circ6'43''$, $\beta\ 76^\circ8'29''$, $\gamma\ 99^\circ42'44''$, D 2.290].

3:5-Di-iodo-1-nitrobenzene (from the di-iodonitroaniline above described by diazotisation in alcoholic solution in presence of sulphuric acid) forms slightly yellow prisms, m. p. 104.5°. When reduced with ferrous sulphate and ammonia it gives 3:5-di-iodoaniline (colourless needles, m. p. 110°).

5-Chloro-1:3-di-iodobenzene is obtained from 4-chloro-2:6-di-iodoaniline, and forms lustrous, colourless needles, m. p. 101°.

5-Bromo-1:3-di-iodobenzene (similarly obtained) crystallises in long needles, m. p. 140°.

1:3:5-Tri-iodobenzene (from 2:4:6-tri-iodoaniline, m. p. 185.6°, or from *s*-di-iodoaniline, m. p. 110°) forms opaque, colourless needles, m. p. 184.2°.

4-Chloro-3:5-di-iodo-1-nitrobenzene (prepared by the action of cuprous chloride on the nitrate of the diazo-compound from 4:6-di-iodo-2-nitro-

aniline) crystallises in almost colourless needles, m. p. 110°. Reduction of this compound is best effected with an alcoholic solution of ammonium sulphide; a small quantity of a sulphur compound is formed at the same time. 2-Chloro-1:3-di-iodobenzene is obtained by decomposing the diazo-salt of this amino-compound with absolute alcohol; it forms thin, rhombic plates, m. p. 82°.

4-Bromo-3:5-di-iodo-1-nitrobenzene (from the nitrate of the diazo-compound of the di-iodonitroaniline and cuprous bromide) forms almost colourless needles, m. p. 125.4°, and crystallises from benzene with $1C_6H_6$ in prisms.

3:4:5-Tri-iodo-1-nitrobenzene (from di-iodonitroaniline by way of the diazo-compound) crystallises in shining yellow prisms. It is reduced (with difficulty) to the corresponding aniline by ferrous sulphate and ammonia, and when this is treated with an alcoholic solution of ethyl nitrite, 1:2:3-tri-iodobenzene (m. p. 116°) is obtained, identical with that from 2:6-di-iodoaniline (m. p. 122°; Körner and Bellasio, A., 1908, i, 778).

2-Chloro-6-bromo-4-nitroaniline is obtained by treating 2-chloro-4-nitroaniline with the calculated quantity of bromine; it forms yellow needles, m. p. 177.4°. The monoacetyl derivative crystallises in pale straw-coloured needles, m. p. 224°, and the diacetyl derivative, tabular prisms, m. p. 139° [prismatic class of the monoclinic system, $a:b:c = 1.1127:1:0.8509$, $\beta = 70.36^\circ$, $D = 1.749$].

3-Chloro-5-bromo-1-nitrobenzene (from 2-chloro-6-bromo-4-nitroaniline by means of ethyl nitrite) crystallises in thin plates, m. p. 81.2°. On reduction with tin and hydrochloric acid it yields 3-chloro-5-bromoaniline (colourless needles or prisms), from which 1-chloro-5-bromo-3-iodobenzene can be prepared by way of the diazo-compound; it forms lustrous needles, m. p. 85.8°, and can also be obtained from 4-chloro-2-bromo-6-iodoaniline, which crystallises in needles, m. p. 110.5°.

3:4-Dichloro-5-bromo-1-nitrobenzene (from the corresponding chlorobromonitroaniline already described) forms yellow prisms, m. p. 82.4°.

5-Chloro-3:4-dibromo-1-nitrobenzene (similarly prepared) crystallises in yellow prisms, m. p. 99.5°. The corresponding 3-chloro-1:2-dibromobenzene (prepared by replacing $-NH_2$ by $-Br$ in 2-chloro-3-bromoaniline) forms rhombic plates, m. p. 72.6°.

3-Chloro-5-bromo-4-iodo-1-nitrobenzene (prepared in a similar way to its analogues above described) crystallises in lustrous needles, m. p. 159°.

2-Chloro-6-iodo-4-nitroaniline (from 2-chloro-4-nitroaniline and iodine chloride) forms pale yellow needles, m. p. 195°. Its monoacetyl derivative forms needles or prisms, m. p. 207°, and the diacetyl derivative, m. p. 113°, prisms of the monoclinic system [$a:b:c = 1.038:1:0.799$, $\beta = 71.44^\circ$, $D = 1.913$].

By elimination of the amino-group the preceding aniline yields 3-chloro-5-iodo-1-nitrobenzene, which forms bundles of prisms, m. p. 70.4°.

3:4-Dichloro-5-iodo-1-nitrobenzene (from the above-described aniline) crystallises in pale yellow prisms, m. p. 59°. It is not possible to obtain the corresponding aniline by reduction. Ammonia and ferrous sulphate reduce it very slowly, tin and hydrochloric acid yield

3-chloro-5-iodoaniline (colourless plates, m. p. 69·6°), whilst ammonium sulphide in alcoholic solution gives 3:4-dichloroaniline.

3-Chloro-4-bromo-5-iodo-1-nitrobenzene (prepared like the analogous compound above described) crystallises in almost colourless needles, m. p. 95°.

5-Chloro-3:4-di-iodo-1-nitrobenzene (from 2-chloro-6-iodo-4-nitroaniline) forms almost colourless needles, m. p. 146·5°.

2-Bromo-6-iodo-4-nitroaniline (from 2-bromo-4-nitroaniline and iodine chloride) crystallises in pale yellow needles, m. p. 221°. The monoacetyl derivative forms yellow prisms, m. p. 226°, and the diacetyl derivative, m. p. 134°, stout prisms of the pinacoidal class of the triclinic system [$a:b:c = 0·9470:1:0·7288$, $\alpha = 83°59'54''$, $\beta = 77°30'18''$, $\gamma = 99°6'14''$, $D = 2·112$].

3-Bromo-5-iodo-1-nitrobenzene (from the preceding aniline) forms thin, flat needles, m. p. 97·5°.

4-Chloro-3-bromo-5-iodo-1-nitrobenzene (from the above-described bromoiodonitroaniline) crystallises in yellow prisms, or in colourless needles, m. p. 84°.

R. V. S.

Preparation of Benzylamine. MARTIN O. FORSTER and HILDA M. JUND (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 118).—A cheap laboratory process for the preparation of benzylamine hydrochloride is described. Benzyl chloride is occasionally shaken during three days with sodium azoimide in spirit, the benzylazoimide is extracted with ether, and, without purification, reduced by means of zinc dust and 50% acetic acid.

J. C. W.

Salts of Dibasic Organic Acids with o-, m-, and p-Toluidine, and with m-4-Xylidine. F. GRÜNWAHD (*J. pr. Chem.*, 1913, [ii], 88, 168—179).—The three toluidines and m-4-xylidine combine with malonic, succinic, malic, tartaric, and fumaric acids in aqueous solution to form acid salts. Attempts to prepare the normal salts were unsuccessful.

o-Toluidine hydrogen malonate crystallises in short prisms (decomp. 108°); the m-toluidine salt in colourless prisms (decomp. 93°). The corresponding hydrogen succinates also crystallise in prisms (decomp. 66° and 121° respectively).

o-Toluidine hydrogen maleate forms leaflets (decomp. 120°); the isomeric m- and p-toluidine salts, colourless needles (decomp. 103° and 153°). o-Toluidine hydrogen fumarate crystallises in hexagonal leaflets (decomp. 150°); the m- and p-toluidine salts in colourless prisms (decomp. 165° and 175°).

Of the salts of m-4-xylidine, the hydrogen malonate forms thin needles (decomp. 93°), the hydrogen succinate, large prisms (decomp. 86°), the hydrogen tartrate, prisms (decomp. 170°), and the hydrogen fumarate, leaflets (decomp. 178°).

When heated with cupric oxide, an aqueous solution of m-toluidine hydrogen oxalate yields cupric m-toluidine oxalate, $\text{Cu}(\text{C}_6\text{H}_4\text{O}_4)_2$, which separates with $3\text{H}_2\text{O}$ in crystals resembling copper sulphate; the acid oxalates of o- and p-toluidine do not form similar copper salts.

Cupric o-toluidine malonate, $\text{Cu}(\text{C}_{10}\text{H}_{13}\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$, forms bluish-green

crystals, which become anhydrous and green at 100°. *Cupric m-toluidine malonate* separates with 3H₂O in steel-blue crystals; the anhydrous salt is green. *Cupric p-toluidine malonate* crystallises with 1H₂O. *Cupric m-4-xylidine malonate*, Cu(C₁₁H₁₄O₄)₂·3H₂O, forms blue leaflets.

The acid toluidine succinates do not yield normal cupric salts.

When boiled with nickel hydroxide in aqueous solution, *o*-toluidine hydrogen malonate yields a *nickel* salt, which forms green crystals containing 6H₂O; *nickel m-toluidine malonate*, Ni(C₁₀H₁₃O₄)₂, crystallises with 4H₂O in reddish-violet leaflets; *nickel p-toluidine malonate* forms green, rhombic leaflets containing 2H₂O.

Nickel m-4-xylidine malonate separates in dove-grey crystals containing 4H₂O. F. B.

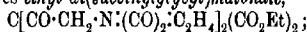
Interactions with Succinylglycyl Chloride and Hippuryl Chloride. JOHANNES SCHEIBER and HANS RECKLEBEN (*Ber.*, 1913, 46, 2412—2420).—*Succinylglycine*, C₂H₄ <math display="block">\begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{N} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}, is prepared by heating molecular proportions of succinic anhydride and glycine at 170—180°; the colourless crystals have m. p. 113°.

With phosphorus pentachloride, colourless needles, m. p. 76°, of *succinylglycyl chloride* are obtained.

The chloride reacts with aniline, forming *succinylglycylanilide*, which crystallises in colourless needles, m. p. 151°.

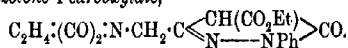
With benzene and aluminium chloride, *succinyliminoacetophenone*, C₂H₄·(CO)₂·N·CH₂·COPh, is formed; it separates in colourless needles, m. p. 143—144°, and yields a colourless *phenylhydrazine*, m. p. 201°.

Condensation of succinylglycyl chloride with ethyl sodiomalonate in boiling ether gives *ethyl di(succinylglycyl)malonate*,



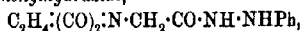
it separates in colourless platelets, m. p. 107°, and gives no coloration with ferric chloride.

Phenylhydrazine converts it into *ethyl 1-phenyl-3-succinylimido-methyl-5-pyrazolone-4-carboxylate*,



This crystallises in matted needles, m. p. 157°, giving a bluish-red coloration with ferric chloride.

Succinylglycylphenylhydrazide,



forms colourless needles, m. p. 213°.

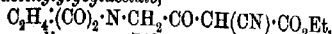
A second product of the condensation is *ethyl succinylglycylmalonate*, C₂H₄·(CO)₂·N·CH₂·CO·CH(CO₂Et)₂, which forms colourless needles, m. p. 55°.

Succinylglycyl chloride and ethyl sodioacetoacetate condense to *ethyl succinylglycylacetoacetate*, of which the colourless needles have m. p. 102°.

Condensation with sodium acetylacetone leads to two products. *Succinylglycylacetylacetone*, C₂H₄·(CO)₂·N·CH₂·CO·CH(COMe)₂, forms

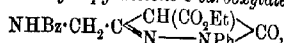
needles, m. p. 122°. *Di(succinylglycyl)acetylacetone* also yields needles, m. p. 150°.

Ethyl cyanosuccinylglycylacetate,



forms colourless needles, m. p. 73°.

Hippuryl chloride and ethyl sodiomalonate condense to a derivative of 2:5-diketo-1:4-dibenzoylpiperazine and ethyl hippurylmalonate, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CO}_2\text{Et})_2$. The latter has m. p. 85°, and shows a positive ferric chloride reaction. With phenylhydrazine, ethyl 1-phenyl-3-benzamidomethyl-5-pyrazolone-4-carboxylate,



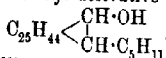
is obtained, m. p. 122—123°. It forms a well characterised, crystalline sodium salt. The above derivative of 2:5-diketo-1:4-dibenzoylpiperazine has m. p. 116°; it dissolves in sodium carbonate, and on precipitation with acid, a substance, m. p. 137°, is obtained containing $\frac{1}{2}\text{H}_2\text{O}$ less, and likewise giving a bluish-violet ferric chloride reaction; on crystallising the compound m. p. 137° from ethyl alcohol, the substance of m. p. 116° is obtained. The latter is regarded as a condensation of two molecules of the piperazine with a molecule of water.

O-Hippurylacetylacetone, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COMe}$, crystallises in platelets, m. p. 109°.

Ethyl cyanohippurylacetylacetate, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, forms colourless needles, m. p. 139°. The additive product with phenylhydrazine has m. p. 107°.

E. F. A.

Cholesterol. XVII. α -Cholestanol. ADOLF WINDAUS and C. UEBIG (*Ber.*, 1913, **46**, 2487—2491).— α -Cholestanol yields on oxidation a ketonic acid, $\text{C}_{27}\text{H}_{46}\text{O}_3$. This is not in agreement with the usual formula $\text{C}_{27}\text{H}_{48}\text{O}$ for cholestanol, and it is proved that the analytical data, particularly of cholestyl chloride and bromide, agree with the formula $\text{C}_{27}\text{H}_{46}\text{O}$ or $\text{C}_{32}\text{H}_{58}\text{O}$. Apparently on treatment of cholesterol with sodium and amyl alcohol, condensation and ring closure to a saturated compound takes place. Accordingly, cholestanol is not a dihydrocholesterol, but an isoamyl derivative of cholesterol,



Cholestyl bromide crystallises in hexagonal platelets, m. p. 118°.

Ketcholestanolcarboxylic acid, $\text{C}_{25}\text{H}_{44}\begin{matrix} \swarrow \text{CO}_2\text{H} \\ \searrow \text{CO}\cdot\text{C}_5\text{H}_{11} \end{matrix}$, separates in long, slender needles which sinter at 110°, m. p. 125°. The *semicarbazone* crystallises in long needles, m. p. 207°.

E. F. A.

Isomeric Naphthenic Acids. FRANK W. BUSHONG and I. W. HUMPHREY (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 57—67).—A quantity of commercial naphthenic acid from Baku, which contained about 50% of water and 5% of illuminating oils, was fractionally esterified. Several portions of 2 litres were heated with 200 c.c. of alcohol and 400 c.c. of sulphuric acid until the temperature rose to 140°, when a further 200 c.c. of alcohol was slowly run in. The distillate

was saponified, the hydrocarbons were removed by steam distillation, and, finally, the naphthenic acids were liberated and converted into methyl esters. These were fractionated and the constants of twenty-six fractions are given. The fraction 165—170° contained methyl hexanaphthenecarboxylate; fraction 189—192°, methyl heptanaphthenecarboxylate; fraction 210—212°, methyl octanaphthenecarboxylate, and fraction 220—224°, methyl nonanaphthenecarboxylate. The densities of the fractions rise continuously with the exception of fraction 200—204°, which agrees with the formula $C_8H_{15}\cdot CO_2Me$, and thus contains a methyl *isooctanaphthenecarboxylate*.

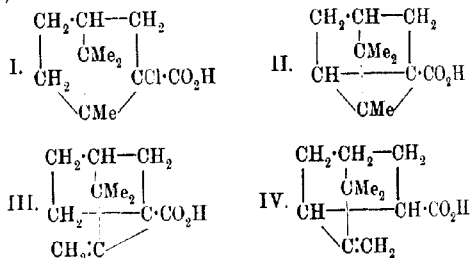
The residual, partly esterified naphthenic acids were then distilled in a current of natural gas from a copper still, when 40% passed over below 285° and 10% between 285—295°. The lower-boiling ethyl esters were redistilled and the fractions boiling below 235° were saponified, freed from hydrocarbons, and the naphthenic acids were finally separated into eighteen fractions. By means of diagrams it is shown that the optical-rotation curve for the acids is parallel to the curve for the methyl esters. The cause of the activity of petroleum is thus due to the naphthenic acids and not to impurities. The maximum levorotation is exhibited by the hexanaphthenecarboxylic acid and its ester.

J. C. W.

The Condensation of Aromatic Aldehydes with Pyruvic Acid. EVA LUBRZYNSKA and IDA SMEDLEY (*Biochem. J.*, 1913, 7, 375—379).—A full account of work of which an abstract has already appeared (*P.*, 1913, 29, 174).

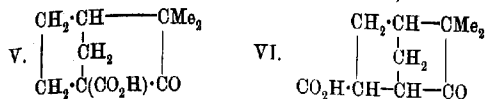
W. D. H.

Camphenecarboxylic Acids and the Constitution of Camphene. JOSEF HOUBEN and ERNST WILLFROTH (*Ber.*, 1913, 46, 2283—2299).—If Wagner's views with respect to the formation of camphene by the loss of hydrogen chloride from bornyl chloride are correct, the intermediate compound (II), formed by a similar removal of hydrogen chloride from α -chloro*allo*camphanecarboxylic acid (I), should give rise to two isomeric camphanecarboxylic acids (III and IV):



The authors find that two isomeric unsaturated acids of this composition are formed when the methyl ester of α -chloro*allo*camphanecarboxylic acid is heated with methyl-alcoholic potassium hydroxide, although only one of them could be isolated in a state of purity.

On oxidation, the camphanecarboxylic acids should be transformed into α - and β -camphenilonecarboxylic acids (V and VI).



Oxidation of the acids formed by the removal of hydrogen chloride from chloroallocamphanecarboxylic acid resulted in the formation of two isomeric ketonic acids having the composition of the camphenilonecarboxylic acids. The investigation of these acids is not yet complete; both are very stable and can be distilled without decomposition, whereas α -camphenilonecarboxylic acid, being a β -ketonic acid, should be readily transformed by loss of carbon dioxide into camphenilone. In addition to the above ketonic acids, considerable quantities of hydropinenecarboxylic (*allocamphanecarboxylic*) acid were found amongst the oxidation products. It is probable that this acid was originally present in the mixture of unsaturated acids submitted to oxidation, and was formed by the reducing action of the methyl-alcoholic potassium hydroxide on the methyl ester of α -chloroallocamphanecarboxylic acid.

Hydropinenecarboxylic acid, prepared from pinene hydrochloride by Houbert's method (A., 1906, i, 21), has m. p. 78° , $[\alpha]_D^{25} - 18.26^\circ$ in alcohol, and is converted by phosphorus pentachloride or thionyl chloride into the *chloride*, $\text{C}_{10}\text{H}_{15}\text{COCl}$, which forms a colourless liquid, b. p. $110^\circ/10$ mm., and yields a *methyl ester*, b. p. $119^\circ/18$ mm., and *phenyl ester*, b. p. $187^\circ/14$ mm.

When heated for one hour with phosphorus pentachloride, hydropinenecarboxyl chloride yields α -chloroallocamphanecarboxyl (*chloro-hydropinenecarboxyl*) *chloride*, $\text{C}_{10}\text{H}_{15}\text{ClCOCl}$, which sublimes with partial decomposition into hydrogen chloride and an unsaturated chloride. The chloro-chloride is obtained as a white, camphor-like mass, m. p. $118-119^\circ$, by evaporation of its ethereal solution after shaking with aqueous sodium carbonate. It probably consists of a mixture of two stereoisomerides related to one another as the *endo*- and *exo*-modifications of bornyl chloride. This view is supported by the behaviour of the *methyl ester*, which is obtained by boiling the chloro-chloride with methyl alcohol for fifteen hours, and apparently consists of two stereoisomerides of different stability, one of the isomerides readily losing hydrogen chloride on distillation, whilst the other is stable. The stable (presumably *exo*-) chloro-ester can be isolated from the mixture by repeated distillation under diminished pressure and has b. p. $131^\circ/13$ mm.

α -Chloroallocamphanecarboxylamide, prepared from the chloro-chloride and ammonia in ethereal solution, has m. p. 122° , and when boiled with water loses hydrogen chloride, yielding an unsaturated *amide*, $\text{C}_{10}\text{H}_{15}\text{CO}\cdot\text{NH}_2$, which crystallises in lustrous leaflets, m. p. 210° , and when kept in contact with fuming hydrochloric acid overnight, is transformed into the original chloro-amide.

When boiled with methyl-alcoholic potassium hydroxide, methyl α -chloroallocamphanecarboxylate yields an oil which consists of a

mixture of hydropinenecarboxylic acid and two isomeric *camphene-carboxylic acids*. One of the latter acids has been isolated, and crystallises in needles, m. p. 105°, b. p. 149—151°/11 mm.

From the product of oxidation of the above acid mixture with potassium permanganate in alkaline solution, two isomeric *ketonic (camphenil-oncarboxylic) acids*, $C_{10}H_{14}O_3$, of m. p. 106° and 131°, together with a hydropinenecarboxylic acid of m. p. 71°, were isolated. The last-mentioned acid gave the same copper, lead, ferrous, ferric, mercuric and silver salts, and the same *anhydride* (microscopic, regular octahedra, m. p. 210°, b. p. 228°/16 mm.) as the original hydropinenecarboxylic acid of m. p. 78°, but differed from it in the magnitude and sign of its rotation ($[\alpha]_D^{25}$ 11·29° in alcohol).

The ketonic acid of m. p. 106° forms a *semicarbazone* (decomp. 203°), and when boiled with acetic anhydride yields an *anhydride*, $C_{20}H_{26}O_4$, crystallising in leaflets, m. p. 114°.

F. B.

Ethyl *p*-Bromobenzoylacetate. WILLIAM J. HALE and LAMBERT THORP (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 132—137).—The preparation of dehydro-*p*-bromobenzoylacetate by the method employed by Perkin in the case of the unsubstituted acid (A., 1885, 277) is described.

p-Bromotoluene was oxidised by boiling permanganate to *p*-bromobenzoic acid; this was converted into the chloride, which was then condensed with ethyl sodioacetate, and, finally, the sodium compound of ethyl *p*-bromobenzoylacetate was gently warmed with aqueous ammonia. The resulting ethyl *p*-bromobenzoylacetate, $C_6H_4Br \cdot CO \cdot CH_2 \cdot CO_2Et$, was obtained as a heavy oil, which, in extremely small quantities, gives a deep red colour with ferric chloride. It could not be distilled, and, when boiled in an open tube, it gave a quantitative yield of dehydro-*p*-bromobenzoylacetate acid, $C_6H_4Br \cdot CO \cdot CH < \begin{smallmatrix} CO-O \\ CO-CH \end{smallmatrix} > C \cdot C_6H_4Br$, in the form of small, yellow needles from glacial acetic acid, m. p. 261°. *p*-Bromobenzoylacetate acid, $C_6H_4O_2Br$, was obtained by hydrolysing the ester with cold 3% potassium hydroxide in the form of needle-like plates which decompose at 106—107° into *p*-bromoacetophenone, and give a violet colour with ferric chloride.

J. C. W.

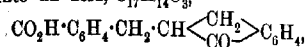
Spirans. III. Attempts to Prepare Optically Active Spirans and Asymmetric Rearrangement. HERMANN LEUCHS and JOHANNES WUTKE (*Ber.*, 1913, 46, 2420—2435. Compare Leuchs and Gieseler, A., 1912, i, 714).—In the preparation of bis-1-hydrindone-2:2-spiran from dibenzylmalonyl chloride, when aluminium chloride serves to eliminate hydrogen chloride, two by-products are obtained. The one, $C_{16}H_{13}Cl$, 1-chloro-2-benzylindene, m. p. 65°, amounts to 14% of the theoretical. The other is a yellow oil identified by means of its phenylhydrazone as 2-benzylhydrindone. Although only 10% have been separated, it amounts to 50% of the theoretical quantity.

When ferric chloride is substituted for aluminium chloride, a much better yield of the bishydrindonespiran is obtained. Its properties

are in accord with the formula $\text{C}_6\text{H}_4 \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$. It forms a diphenylhydrazone and a mono-oxime, and also reacts with two molecules of hydroxylamine, forming a dioxime dihydrate from which the excess of hydroxylamine oxidises away two atoms of hydrogen.

The mono-oxime (m. p. 215°) is converted by phosphorus pentachloride in ethereal suspension into an amide, either 1-hydrindone-dihydrocarbostyryl-2:3-spiran or isocarbostyrylspiran. The mono-oxime shows no tendency to form an isooxazole.

The 2-position of the carbonyl group in the spiran makes it possible to convert it into an acid, $\text{C}_{17}\text{H}_{14}\text{O}_3$,

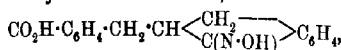


which when heated regenerates the spiran.

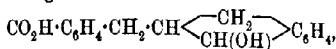
Semicarbazide acetate in cold alcoholic solution converts the spiran into an insoluble mixed hydrazide of the carbamic acid and the acid

$\text{C}_{17}\text{H}_{14}\text{O}_3$, namely, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \\ \text{CON}_2\text{H}_2 \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix} \text{CO} \cdot \text{C}_6\text{H}_4$, from which the free acid is recovered.

Hydroxylamine yields an oximic acid,

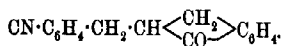


which can be easily reduced with sodium amalgam. Two hydrogen atoms are taken up, and a new asymmetric carbon atom formed, the hydroxy-acid having the formula



and being a mixture of two racemic forms. It does not tend to form an anhydride. The keto-acid is converted into the corresponding acid chloride by means of phosphorus pentachloride; this as low as 60° loses hydrogen chloride, and forms bishydrindonespiran.

Ammonia acts on the spiran to form two compounds—the one, $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}$, representing the amide of the ketonic acid, and the other, $\text{C}_{17}\text{H}_{13}\text{ON}$, being the corresponding nitrile,



This constitution is confirmed by the fact that the action of ammonia on the keto-chloride gives rise to the same amide.

The amide is not hydrolysed by cold concentrated hydrochloric acid, but converted into an anhydride, which is hydrolysed by heating with 70% sulphuric acid at 170° to a spiran-anhydride.

Crystallisation of the brucine salt of the ketonic acid yields a theoretical yield of the optically active *dextro*-salt, both the crystals and the mother liquor being dextrorotatory. It is assumed that the *laevo*-acid salt is enolised and the enol re-converted into the ketonic *d*-salt, since the equilibrium is determined entirely in this direction owing to the crystallisation of the *d*-salt as fast as it is formed.

The transformation is an instance of asymmetric rearrangement

rather than of autoracemisation, since the optically inactive enol gives rise exclusively to an optically active acid.

The *d*-ketonic acid slowly but completely loses its activity on keeping in chloroform solution, and still more quickly in neutral or alkaline aqueous solution, owing to conversion into the enol.

An optically active bishydrindonespiran could not be obtained by eliminating hydrogen chloride from the active keto-chloride.

Bishydrindonespirandioxime dihydrate forms colourless, slender needles, m. p. 175° (decomp.).

The Beckmann rearrangement product, $C_{17}H_{13}O_3N$, of the mono-oxime separates in long, colourless needles, m. p. 255° (decomp.); it gives no ferric chloride reaction.

The mixed *hydrazide* from the spiran and carbamic acid, $C_{15}H_{11}O_3N$, crystallises in short needles, m. p. 245° (decomp.).

The *oxime* of 1-hydrindone-2-benzyl-*o*-carboxylic acid forms dome-like prisms, m. p. 188° (decomp.).

The *amide*, prepared from the keto-chloride by the action of ammonia, has m. p. $138-140^{\circ}$, crystallising in massive, four-sided platelets.

The *brucine* salt of the *dextro*-ketonic acid forms transparent, massive crystals, m. p. $180-183^{\circ}$. The acid derived from it has $[\alpha]_D^{20} + 64^{\circ}$ in chloroform. The pure active acid could not be obtained—a product evaporated at 20° had m. p. $128-141^{\circ}$, $[\alpha]_D^{20} + 56^{\circ}$. In benzene the pure acid had $[\alpha]_D^{20} + 79^{\circ}$; it racemises here more quickly than in chloroform.

E. F. A.

Spirans. IV. Stereochemical Treatment of the Keto-Enol Question. HERMANN LEUCHS (*Ber.*, 1913, 46, 2435–2442. Compare Lapworth, T., 1904, 85, 30; K. H. Meyer, A., 1911, i, 350, 940).—1-Hydrindone-2-benzyl-*o*-carboxylic acid when treated with bromine in chloroform solution readily forms a brominated ketonic acid, $CO_2H \cdot C_6H_4 \cdot CH_2 \cdot CBr \cdot \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} > C_6H_4$. Proof of this structure is

afforded by the fact that on heating with ammonium hydroxide, the bromine is displaced and a lactone formed, namely, *dihydroisocoumarin-1-hydrindone-3 : 2-spiran*, $C_8H_4 \cdot \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ CO \cdot O \end{smallmatrix} \cdot C \cdot \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} > C_6H_4$.

If in the process of bromination the first stage is the formation of an enol, $CO_2H \cdot C_6H_4 \cdot CH_2 \cdot C \cdot \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ C(OH) \end{smallmatrix} > C_6H_4$, which contains no asymmetric carbon atom, then on bromination of the optically active 1-hydrindone-2-benzyl-*o*-carboxylic acid, an optically inactive product should result.

Actually an optically active ($[\alpha]_D + 6.5^{\circ}$) product is obtained containing much inactive brominated keto-acid. Heating with sodium carbonate changes the sign of the rotation, and it was possible to isolate the pure 1-*dihydroisocoumarin-1-hydrindone-3 : 2-spiran*, which crystallises in lustrous needles, m. p. $175-176^{\circ}$, $[\alpha]_D^{20} - 65.3^{\circ}$.

This is the first optically active substance in which the spiran carbon atom is the asymmetric centre.

Bromination of ketones does not in consequence necessarily involve the intermediate formation of enol; in this case about 5–10% of

the brominated product is optically active. It is considered that even in this instance the greater part of the bromination involves the intermediate formation of the enol, and that this will be still more the case with substances which are more easily enolised.

2-Bromo- α -hydrindone-2-benzyl-o-carboxylic acid forms colourless crystals pointed at one end, m. p. 154° ; they are converted into the lactone on fusion.

Dihydroisocoumarin-1-hydrindone-3:2-spiran crystallises in needles or prisms, m. p. $153\text{--}154^{\circ}$. E. F. A.

Studies in Esterification. V. Esterification of Amides and Thioamides and the Formation of Dithio-esters. F. EMMET REID (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 423—430. Compare A., 1909, ii, 650; 1910, i, 481; 1911, i, 199; ii, 477).—In earlier papers it has been shown with reference to esterification that benzamide is the analogue of benzoic acid, and that mercaptan is the analogue of alcohol. It is now shown that benzamide can be esterified by mercaptan, and thiobenzamide by alcohol or mercaptan.

Ethyl thiolbenzoate is readily decomposed into mercaptan and benzamide by the action of ammonia at 20° , whereas ethyl benzoate reacts but slowly with ammonia even at 200° . Benzamide is readily esterified in presence of hydrochloric acid, which not only catalyses the reaction, but also combines with the ammonia so that the action proceeds to completion, and it was therefore expected that hydrogen chloride would similarly accelerate the esterification of benzamide by mercaptan. On heating benzamide in a sealed tube at 100° with mercaptan, saturated with hydrogen chloride at -20° , ethyl thiolbenzoate and ammonium chloride were produced. Thiobenzamide unites with about 1.5 mols. of hydrogen chloride to form an amber-coloured liquid, whilst other thioamides combine with about 1 mol.

Ethyl dithiobenzoate can be prepared by treating thiobenzamide, saturated with dry hydrogen chloride at 0° , with rather more than the calculated amount of mercaptan, and leaving the mixture in a sealed tube for about five weeks; the ester has b. p. $180^{\circ}/28$ mm., D_{25}^{25} 1.1477, D_4^{25} 1.1439, apparent coefficient of expansion $0\text{--}25^{\circ}$, 0.000699, molecular volume, 159.28, viscosity at 25° , 0.03117, and fluidity at 25° , 32.09. These constants are compared with those of ethyl benzoate and ethyl thiolbenzoate. Ethyl dithiobenzoate is readily transformed into thionbenzamide by alcoholic ammonia at the ordinary temperature. The reaction: $\text{Ph}\cdot\text{CS}\cdot\text{NH}_2 + \text{C}_2\text{H}_5\cdot\text{SH} \rightleftharpoons \text{Ph}\cdot\text{CS}\cdot\text{SEt} + \text{NH}_3$ is therefore reversible. E. G.

Action of Potassium Xanthate on Halogen-malonic Acids. EINAR BILMANN and ERIK HOST MÅDSEN (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 339—342).—It has been shown in earlier papers (A., 1905, i, 625; 1906, i, 625, 626) that by the action of potassium xanthate on the halogen derivatives of certain organic acids, xanthyl derivatives are produced which, on treatment with ammonia, are converted into thiol acids. The action of potassium xanthate on bromomalonic, bromoisopropylmalonic, bromoethylmalonic, and bromobenzylmalonic acids has now been studied. These acids yield xanthyl derivatives which are very unstable, and from which pure xanthylmalonic acids

cannot be obtained. On heating the acidified solutions, the corresponding monobasic acids are produced, and in this way xanthylacetic, α -xanthylbutyric, and β -phenyl- α -xanthylpropionic acids have been isolated.

If the solutions of potassium xanthate and alkali halogenmalonates are acidified immediately after they have been mixed, an entirely different reaction takes place and dioxanthyl is produced, thus: $2\text{OEt}\cdot\text{CS}\cdot\text{SK} + \text{R}\cdot\text{CBr}(\text{CO}_2\text{K})_2 + 3\text{HCl} = \text{OEt}\cdot\text{CS}_2\cdot\text{CS}_2\cdot\text{OEt} + \text{R}\cdot\text{CH}(\text{CO}_2\text{H})_2 + \text{KBr} + 3\text{KCl}$.

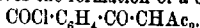
β -Phenyl- α -xanthylpropionic acid, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{S}\cdot\text{CS}\cdot\text{OEt}$, m. p. $89-90^\circ$, prepared by the action of potassium xanthate on sodium α -bromophenylpropionate, forms colourless crystals, and when treated with a mixture of aqueous ammonia and alcohol, is converted into α -thiol- β -phenylpropionic acid, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{SH})\cdot\text{CO}_2\text{H}$, b. p. $184-187^\circ/11-12\text{ mm.}$, m. p. 46° , which forms colourless crystals. By the action of copper sulphate on the alkali salts of this thiol acid, the latter is oxidised to α -disulphido- β -phenylpropionic acid, $[\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO}_2\text{H})]_2\text{S}_2$,

and the cuprous salt of the thiol acid is precipitated. The disulphido-acid can be obtained as a crystalline solid by oxidising the thiol acid with iodine.

E. G.

as-Phthalyl Chloride. JOHANNES SCHEIBER (*Ber.*, 1913, 46, 2366-2370).—The author (A., 1912, i, 542, 559) has shown that the unsymmetrical formula, $\text{C}_6\text{H}_4\langle\text{CCl}_2\text{CO}\rangle\text{O}$, proposed for phthalyl chloride is untenable on both chemical and physical grounds, and Ott (A., 1912, i, 828) has obtained the isomeric asymmetric form of phthalyl chloride. The behaviour of the new chloride towards compounds of the type of ethyl sodioacetoacetate and towards ammonia has been now studied as well as the ultra-violet absorption spectra.

Both chlorides behave similarly with ethyl acetoacetate, since in each case reaction involves the formation of a compound



Hence the behaviour of such chlorides with sodium acetoacetate as also with ammonia gives no clue as to their structure.

Both chlorides give exclusively *o*-cyanobenzoic acid with ammonia, but the new asymmetric chloride reacts more slowly. There is thus a considerable difference in the stability of the complexes $\text{C}_6\text{H}_4\langle\text{CCl}_2\text{SO}_2\rangle\text{O}$

and $\text{C}_6\text{H}_4\langle\text{CCl}_2\text{CO}\rangle\text{O}$. The asymmetric chloride absorbs less strongly than phthalic acid or its esters in the ultra-violet.

E. F. A.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and Their Use for Synthetical Operations. IX. EMIL FISCHER and MAX RAPAPORT (*Ber.*, 1913, 46, 2389-2401).—In part already abstracted (this vol., i, 731).

[With H. STRAUSS.]—Trimethylcarbonatophloroglucinolcarboxylic acid, obtained on treating phloroglucinolcarboxylic acid with methyl chloroformate in presence of dimethylaniline, forms small, colourless prisms,

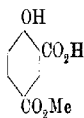
m. p. 122° (decomp.), and no longer shows a bluish-violet coloration with ferric chloride. It is converted into the corresponding chloride by phosphorus pentachloride.

E. F. A.

Pyrimidines. LV. The Catalytic Action of Esters in the Claisen Condensation. TREAT B. JOHNSON and ARTHUR J. HILL (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 147—156 *).—Ethyl phenoxylacetate undergoes a Claisen condensation in ethereal solution in presence of sodium to form the sodium compound of ethyl α -di-phenoxylacetate, $\text{OPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{OPh})\cdot\text{CO}_2\text{Et}$. The same substance was produced in presence of ethyl acetate, and no evidence of the formation of the condensation product of the two esters, namely, ethyl γ -phenoxylacetate, could be obtained. As has since been described (A., 1912, i, 912), the crude sodium salt condenses with thiocarbamide to form 2-thio-5-phenoxy-4-phenoxyethyltetrahydro-6-pyrimidone, and the yield of this insoluble product has been taken as an indication of the extent of the above Claisen condensation under different conditions. It is found that ethyl acetate acts as a catalyst, the addition of 0.5 mol. more than doubling the yield. J. C. W.

Some Derivatives of 4-Hydroxyisophthalic Acid. FRANCIS D. DODGE (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 81—85).—During the steam-distillation of large quantities of methyl salicylate, the author has sometimes obtained, towards the end of the operation, crystals of dimethyl 4-hydroxyisophthalate (Jacobsen, A., 1878, 583). Its presence is ascribed to irregularities in the manufacture of salicylic acid, since 4-hydroxyisophthalic acid may be prepared by the action of carbon dioxide on sodium salicylate at 370° (Ost, A., 1876, 521).

Partial esterification of the acid and also partial hydrolysis of the dimethyl ester lead to the same *mono*-ester, which crystallises in transparent plates with $1\text{H}_2\text{O}$ from diluted alcohol, has m. p. 187° when anhydrous, and gives a reddish-purple coloration with ferric chloride. From the fact that it yields methyl anisate on heating, and according to V. Meyer's ester law, it is the *para*-ester (annexed formula). J. C. W.

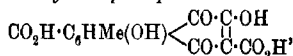


Carminic Acid. OTTO DIMROTH (*Annalen*, 1913, 399, 1—35).—Investigations of the three "insect" dyes, carminic acid, kermesic acid, and laccaic acid, have been carried out concurrently in the expectation, which has been justified, that the results would mutually confirm one another. The structure of kermesic acid, which is the simplest of the three, has been determined (Dimroth and Scheurer, this vol., i, 980). The present paper, however, deals mainly with carminic acid. The remarkable and unexpected result has been established that this acid and kermesic acid are derivatives of an anthraquinone.

[With G. WEURINGH and L. HOLCH.]—Carminic acid, isolated from cochineal by Schunck and Marchlewski's process (it is advantageous, however, to decompose the lead lake by sulphuric acid and methyl, not

* and *J. Amer. Chem. Soc.*, 1913, 35, 1023—1034.

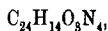
ethyl, alcohol), is oxidised by hydrogen peroxide and aqueous sodium hydroxide in the presence of a little cobalt sulphate as catalyst, whereby carminoquinone is formed as a labile intermediate product, the final product, after acidification with 80% acetic acid, being a sparingly soluble *sodium hydrogen salt*, $C_{28}H_{18}O_{10}Na_2 \cdot 5H_2O$, yellow crystals. By trituration with dilute hydrochloric acid at 0° and crystallisation of the product from cold ethyl acetate, this salt yields 2:6-dihydroxy-8-methyl- α -naphthaquinone-3:5-dicarboxylic acid,



a pale yellow, extremely hygroscopic, crystalline powder, which forms a *sodium salt*, $C_{13}H_5O_8Na_2 \cdot 4H_2O$, orange needles, and yields carminazarin by oxidation with potassium permanganate and sulphuric acid. The orientation of the substituents in the dicarboxylic acid is determined by its oxidation to carminazarin and by the colour reactions of the acid—which are identical with those of 2:6-dihydroxy- α -naphthaquinone (compare Dimroth and Kerkovius, following abstract). By gentle warming with water, the acid loses carbon dioxide and yields 2:6-dihydroxy-8-methyl- α -naphthaquinone-5-carboxylic acid,

$C_{12}H_6O_6$, brownish-yellow needles (*potassium salt*, $C_{12}H_7O_6K$, citron-yellow needles; *dipotassium derivative*, $C_{12}H_6O_6K_2$, orange-red crystals), which develops a red coloration with alkalis, brownish-yellow with concentrated sulphuric acid, and brownish-red with alcoholic ferric chloride. The monocarboxylic acid, which is obtained more conveniently by heating the sodium hydrogen derivative of the dicarboxylic acid with *N*-hydrochloric acid on the water-bath, reacts with bromine in glacial acetic acid at 40° to form 7-bromo-2:6-dihydroxy-8-methyl- α -naphthaquinone-5-carboxylic acid, $C_{12}H_5O_6Br$, m. p. $240-244^\circ$, yellow needles. The brominated acid forms α -bromocarmin by treatment with hydrobromic acid, and Will and Leymann's β -bromocarmin by treatment with bromine in cold methyl alcohol; the latter is thus definitely proved to be 3:5:7-tribromo-2:6-dihydroxy-8-methyl- α -naphthaquinone.

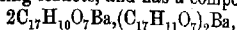
The constitution, 2:3:6-trihydroxy-8-methyl- α -naphthaquinone-5-carboxylic acid, previously ascribed by the author to carminazarin, is supported by the fact that its oxidation product, carminazarinquinone, reacts with alcoholic *o*-phenylenediamine to form a *diphenazine*,



yellow needles, the *acetyl derivative*, $C_{28}H_{18}O_4N_4$, of which still forms a sparingly soluble *sodium salt*.

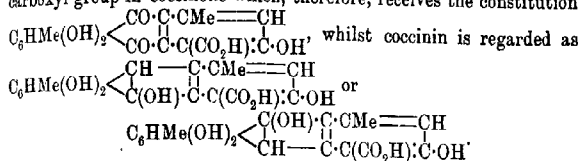
[With B. KERKOVIVS.]—The largest, well characterised fission product of carminic acid is coccinin, obtained by Hlasiwetz and Grabowski in 1867 by fusing the acid with potassium hydroxide. Prepared at $170-200^\circ$ by a modification of these authors' process, coccinin, $C_{17}H_{14}O_6$, has been obtained as a crystalline substance which forms a *tetra-acetyl derivative*, $C_{25}H_{22}O_{10}$, m. p. $242-244^\circ$, faintly yellow crystals. By oxidation in 6% sodium hydroxide with air or oxygen until the colour of the solution has changed from yellow through green to a pure violet, and then acidifying with hydrochloric acid, coccinin

yields *coccinone*, $C_{17}H_{12}O_7$, dark brown, metallic crystals, which begins to decompose at 250° , and forms a *triacetyl* derivative, $C_{23}H_{18}O_{10}$, m. p. 210° , orange-red crystals, and three *barium* salts, one of which crystallises in glistening leaflets, and has a composition,

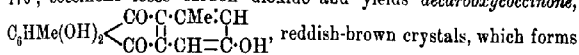


analogous to that of the sodium hydrogen salt of 2:6-dihydroxy-8-methyl- α -naphthaquinone 3:5-dicarboxylic acid. In concentrated sulphuric acid, coccinone develops a violet colour which changes to blue on the addition of boric acid—a reaction similar to those exhibited by most hydroxyanthraquinones.

Coccinone is reduced to coccinin by zinc dust and ammonia, and is oxidised by hydrogen peroxide and aqueous sodium hydroxide below 20° , yielding cochenillic acid and a second, unexamined acid. The author is of opinion that coccinin and coccinone are derivatives of anthranol and of anthraquinone respectively. The formation of cochenillic acid determines the orientation of a hydroxyl, methyl, and carboxyl group in coccinone which, therefore, receives the constitution



By heating with water at 200° or with dilute sulphuric acid at 170° , coccinone loses carbon dioxide and yields *decarboxycoccinone*,



a purplish-red solution in alkalis, and dissolves in concentrated sulphuric acid with a blue colour changing to violet after the addition of boric acid.

[With L. HOLCH.]—The question remains to be discussed whether carminic acid is a derivative of anthraquinone, or whether the anthracene nucleus in coccinin is produced during the fusion of carminic acid with potassium hydroxide. By distillation with zinc dust in a current of hydrogen, carminic acid yields about 5% of a mixture of hydrocarbons which apparently contains anthracene and α -methylanthracene, since in the mixture, after oxidation, anthraquinone has been certainly identified, whilst a substance, m. p. 165° , has also been obtained which has the very characteristic crystalline form of α -methylanthraquinone.

When boiled with dilute sulphuric acid, carminic acid yields about 10% of a *trihydroxymethylanthraquinonecarboxylic acid*, $C_{16}H_{10}O_7$, m. p. above 305° which crystallises in needles, and is converted by water at 230 – 240° into a *trihydroxymethylanthraquinone*, $C_{15}H_{10}O_5$, brick-red needles.

C. S.

2:6- and 2:7-Dihydroxy- α -naphthaquinones. OTTO DIMROTH and BERTHOLD KERKOVICUS (*Annalen*, 1913, 399, 36–43).—By treatment with acetic anhydride containing a few drops of concentrated sulphuric acid, 6-hydroxy- β -naphthaquinone yields 1:3:4:6-tetra-

acetoxynaphthalene, $C_{18}H_{16}O_3$, m. p. 181—182°, colourless leaflets. By hydrolysis with methyl-alcoholic potassium hydroxide, the passage of oxygen through the resulting solution, and acidification, 2:6-dihydroxy-*a-naphthaquinone*, $C_{10}H_6O_4$, yellow crystals, is obtained. It forms a *diacetyl* derivative, yellow leaflets, and dissolves in sodium carbonate and sodium hydroxide with a blood-red colour, and in concentrated sulphuric acid with a brownish-yellow colour. By bromination in glacial acetic acid, 2:6-dihydroxy-*a-naphthaquinone* forms a *tribromo*-derivative, $C_{10}H_4O_4Br_3$, m. p. 283—286°, yellowish-brown crystals, which is converted by bromine in methyl alcohol into 3:5:7-*tribromo*-2:6-dihydroxy-*a-naphthaquinone*, $C_{10}H_2O_4Br_3$, m. p. 242°, yellow crystals; the latter dissolves in sodium carbonate or hydroxide, or in concentrated sulphuric acid, with a reddish-brown colour.

By reactions similar to the preceding, 7-hydroxy-*β-naphthaquinone* has been converted into 1:2:4:7-tetra-acetoxynaphthalene, m. p. 140—141°, colourless crystals, from which 2:7-dihydroxy-*a-naphthaquinone*, decomp. above 200°, orange-yellow needles, has been obtained. The latter dissolves in aqueous sodium hydroxide and in concentrated sulphuric acid with a crimson-red colour, and by bromination in glacial acetic acid yields 3:6:8-*tribromo*-2:7-dihydroxy-*a-naphthaquinone*, m. p. 228—229°, pale yellow prisms, the solution of which in sodium carbonate or hydroxide is much more blue than that of the preceding isomeride.

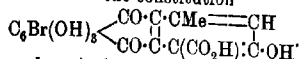
Mention has been made (Dimroth, preceding abstract) of the importance of the preceding colour reactions in connexion with the constitutions of *β-bromocarmin* and of 2:6-dihydroxy-8-methyl-*a-naphthaquinone*-5-carboxylic acid.

C. S.

Kermes Dye. OTTO DIMROTH and WILHELM SCHEURER (*Annalen*, 1913, 399, 43—61).—In addition to kermesic acid, kermes dye contains about 0.06% of a second acid, $C_{18}H_{18}O_6$, which is called *flavokermesic acid*. It crystallises in needles or prisms. In the optical properties of its solutions and as a dye, it shows very little resemblance to kermesic acid, and, therefore, has not been studied thoroughly. The separation of flavokermesic acid from kermesic acid is effected best by utilising the facts that the disodium salt of the latter is almost insoluble in hot 2*N*-sodium acetate, whilst sodium flavokermesate dissolves fairly easily. The presence of flavokermesic acid in kermesic acid is easily detected by the colour of the solution in concentrated sulphuric acid containing boric acid; the solution of the pure acid is a clear blue, that of the impure acid is dull, or a dirty bluish-violet.

When heated with water at 150°, kermesic acid loses carbon dioxide, and is converted into *decarboxykermesic acid*, $C_{17}H_{18}O_7$, red needles, which begins to sublime above 150°, carbonises without melting, is almost insoluble in sodium hydrogen carbonate, and dissolves in aqueous sodium hydroxide and in concentrated sulphuric acid containing boric acid, forming solutions which have the same colours as the corresponding solutions of kermesic acid. Kermesic acid yields *α-bromocarmin* by bromination in boiling 50% acetic acid. When brominated in boiling glacial acetic acid, however, it is converted into

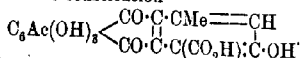
bromococcin, $C_{16}H_9O_8Br$, m. p. 259—260° (decomp.), red needles, which forms a *potassium hydrogen* salt, $C_{16}H_8O_8BrK$, $C_{16}H_9O_8Br$, and a *tetra-acetyl* derivative, $C_{16}H_5O_8BrAc_4$, yellow crystals, and yields cochenillic acid by oxidation with warm alkaline hydrogen peroxide in the presence of a trace of a manganous salt. These results indicate that bromococcin must have the constitution



The three homonuclear hydroxyl groups cannot be in the vicinal position because bromococcin resembles purpurin, not anthragallol, in its dyeing function.

When kermesic acid or bromococcin is brominated in methyl alcohol and the product is treated with concentrated hydrobromic acid, tribromococcin, $OH \cdot C_6MeBr_3 \begin{array}{l} \diagup CO \\ \diagdown CO \end{array} C_6Br(OH)_3$, m. p. 245—248° (decomp.), is obtained, which crystallises from acetic acid in long, red needles. It dissolves in concentrated sulphuric acid with a reddish-violet colour, which changes to deep blue by the addition of boric acid. It forms a *tetra-acetyl* derivative, $C_{13}H_5O_6Br_3Ac_4$, m. p. 223°, greenish-yellow needles, and is converted into nitrococcus acid by fuming nitric acid. A *substance*, $C_{13}H_5O_6Br_3$, yellow needles, is obtained as a by-product in the preparation of tribromococcin.

Kermesic acid, $C_{13}H_{12}O_9$, and bromococcin, $C_{16}H_9O_8Br$, are nearly related substances. Hence from the constitution of the latter, it is very probable that kermesic acid, which does not exhibit the properties of an aldehyde, has the constitution



This deduction is supported, not only by the formation of tribromococcin by bromination, but also by the result of the distillation of kermesic acid with zinc dust. The mixture of hydrocarbons thus obtained contains α -methylanthracene (isolated as the styphnic acid compound, and identified in the form of α -methylanthraquinone) and, probably, anthracene.

[With A. E. SHERNDAL.]—The wax which is obtained in working up the kermes dye is *ceryl cerolate*, $C_{32}H_{104}O_2$, m. p. 81°, colourless leaflets, since it yields ceryl alcohol and cerotic acid by hydrolysis.

C. S.

Stick-lac Dye. OTTO DIMROTH and STEPHAN GOLDSCHMIDT (*Annalen*, 1913, 399, 62—90).—Stick-lac or gum-lac contains, embedded in resin, wax, and other substances, a small quantity of a red dye similar to cochineal. The dye has been called laccaic acid. It is not, as supposed formerly, identical with carminic acid, but the two are closely related, giving solutions in alkalis of the same colour and exhibiting the same spectrum; the characteristic absorption bands shown by the two acids in concentrated sulphuric acid, however, are differently situated in the two spectra.

Laccaic acid is isolated as follows: Stick-lac is digested with water at 50°, the clear red solution when cold, is acidified with acetic acid,

decanted from the precipitated resin, evaporated to a small bulk, and acidified with hydrochloric acid; the crude laccic acid thus obtained is crystallised from hot 85% formic acid, washed, dried at 60–70°, and finally crystallised from hot dilute hydrochloric acid. It has the formula $C_{20}H_{14}O_{10}$, not $C_{18}H_{12}O_8$ as stated in the literature, crystallises in dark red, microscopic rhombohedra, decomposes and yields a trace of a red sublimate when heated, and does not form crystalline salts except a sodium hydrogen salt, $C_{20}H_{12}O_{10}Na_2$, $C_{20}H_{13}O_{10}Na$. Its dyeing properties are similar to those of carminic acid. Laccic acid neutralises five equivalents of barium hydroxide, and when treated with acetic anhydride and a few drops of concentrated sulphuric acid yields a triacetyl derivative, $C_{20}H_{20}O_{13}$, $C_2H_4O_2$, m. p. 176°, reddening at about 160°, yellow, microscopic needles (from acetic acid).

By reduction with tin and hydrochloric acid or with zinc dust and boiling aqueous ammonia, laccic acid is converted into a substance, $C_{20}H_{14}O_9$, brownish-yellow rhombohedra, which is oxidised by hydrochloric acid and cupric chloride to a substance, $C_{20}H_{14}O_8$, which differs from laccic acid in its colour reactions; the substances $C_{20}H_{16}O_8$ and $C_{20}H_{14}O_9$ are probably related as quinol and quinone.

An alkaline solution of laccic acid is readily oxidised by hydrogen peroxide in the presence of a trace of a cobalt, manganese, cerous, or ferrous salt. When one molecular proportion of hydrogen peroxide is used, the solution contains an unstable intermediate oxidation product, since by acidifying the solution and adding sulphurous acid, laccic acid is recovered. The complete oxidation requires 2.5 to 3 molecular proportions of hydrogen peroxide, manganous chloride being the best catalyst. The oxidation product thus obtained is calaic acid, $C_{18}H_{11}O_{11}$, which crystallises from ether in small, yellow prisms containing ether of crystallisation and from water in needles containing $2\frac{1}{2}H_2O$. Calaic acid contains three carboxyl groups and one carbonyl group, does not possess dyeing properties, and forms a crystalline barium salt (by means of which it is best purified) and a silver salt, $C_{18}H_{11}O_{11}Ag_2$.

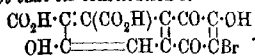
By bromination in glacial acetic acid, calaic acid yields two products. One of these is an α -ketonic acid, $C_{12}H_9O_8Br$, m. p. 208–209°, brownish-yellow crystals, which forms a phenylhydrazone and semicarbazone, develops a dirty reddish-violet coloration with ferric chloride, and by treatment with methyl-alcoholic hydrogen bromide yields an additive compound of the methyl ester, $C_{18}H_{12}O_8Br_2 \cdot HBr$, m. p. 133–134° (decomp.), colourless needles. When heated with concentrated sulphuric acid at 80–90°, the ketonic acid loses carbon monoxide and yields an acid, $C_{11}H_9O_5Br_2$, m. p. 245–246° (decomp.), which is monobasic and develops an intense violet coloration with ferric chloride.

The second and more important product of the bromination of calaic acid is β -bromolaccain, $C_{12}H_9O_8Br$, which is separated from the other product by means of its solubility in cold acetone. β -Bromolaccain has m. p. 234–235° (decomp.), separates from aqueous solution in stout crystals containing $2H_2O$, and forms a potassium salt,

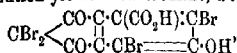
$C_{11}H_9O_8BrK_4H_2O$, hexagonal plates. It develops a deep red coloration with ferric

chloride, dyes wool reddish-yellow in an acid-bath, and by treatment with acetic anhydride and concentrated sulphuric acid forms *diacetyl-β-bromolaccain anhydride*, $C_{18}H_7O_5Br$; the last reaction proves that β-bromolaccain contains two carbonyl groups in the ortho-position and two hydroxyl groups.

Since β-bromolaccain presents in its behaviour a close analogy to β-bromocarmin and resembles 2:6-dihydroxy-α-naphthaquinone in its colour reactions (Dimroth and Kerkovius, preceding abstract), there can be little doubt that its constitution is

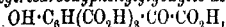


This is supported by the following evidence. Just as β-bromocarmin yields the indone derivative, α-bromocarmin, so β-bromolaccain in boiling aqueous solution yields with bromine, α-bromolaccain,



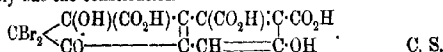
colourless needles, which decomposes when heated and yields bromoform and 2:6-dibromophenol-3:4:5-tricarboxylic acid, m. p. 257–258°, by treatment with sodium hypobromite; the tricarboxylic acid develops only a faint coloration with ferric chloride (therefore, the hydroxyl group is not in the ortho-position to a carboxyl group) and as a phthalic acid derivative yields a yellow dye by fusion with resorcinol and zinc chloride.

The constitution of β-bromolaccain is also supported by the fact that oxidation by hydrogen peroxide in glacial acetic acid on the water-bath produces *hydroxytricarboxyphenylglyoxylic acid*,



n. p. 229.5–230° (decomp.), flattened plates, which develops a brown-shed coloration with ferric chloride and is converted into a *phenol-tricarboxylic acid*, m. p. 212–214° (decomp.), quadratic crystals, by concentrated sulphuric acid at 130–140°.

A by-product of the oxidation of β-bromolaccain is a *substance*, $C_{12}H_5O_5Br_2$, m. p. 188–190° (decomp.), which readily loses bromine and probably has the constitution



[Angeli-Rimini Reaction of the Aldehydes.] ANGELO ANGELI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 851–854).—A reply to Balbiano (this vol., i, 733). R. V. S.

The New Decomposition of the Oximes. ANGELO ANGELI and LEON ALESSANDRI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 735–744. Compare Angeli, A., 1912, i, 269).—Benzophenoneoxime decomposes rapidly at about 180°, yielding benzophenone, nitrogen and ammonia. The decomposition occurs at a lower temperature (140°) in presence of copper oxide, whilst with cuprous chloride it begins a little above 100°. It was not possible to isolate a copper salt, but the silver salt was prepared. It is stable when dry, but if kept in a moist state in

the absence of air it evolves pure nitrogen, and benzophenone is formed at the same time.

The *silver* salt of piperonaldehydeoxime behaves similarly.

Fluorenoneoxime also decomposes at its m. p. (194°); the gas evolved contains nitric oxide as well as nitrogen, even when the decomposition is effected in the absence of air.

The mixture of stereoisomeric oximes prepared from phenyl *p*-tolyl ketone (m. p. about 120°) decomposes above 200° in a like manner, nitric oxide being also formed.

In the case of deoxybenzoinoxime and acetophenoneoxime decomposition is slight when the pure substance is heated, but becomes considerable in presence of cuprous chloride or of cupric oxide.

Benzophenoneoxime, phenyl *p*-tolyl ketoneoxime, and acetophenoneoxime are apt to decompose spontaneously on keeping. R. V. S.

Phototropy. FERDINANDO GRAZIANI and F. BOVINI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 793—797).—The authors have prepared a number of diphenylhydrazones and *p*-ditolylhydrazones, none of which is phototropic. In some cases in which the compounds had been previously prepared, the m. p.'s were found somewhat different from those given in the literature. Benzaldehydediphenylhydrazone has m. p. 125°.

Anisaldehydediphenylhydrazone, $\text{NPh}_2 \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, forms colourless crystals, m. p. 76°.

Cuminaldehydediphenylhydrazone has m. p. 80—81°.

Salicylaldehydediphenylhydrazone has m. p. 139—140°.

Benzaldehyde-p-ditolylhydrazone, $\text{N}(\text{C}_7\text{H}_7)_2 \cdot \text{N} : \text{CHPh}$, crystallises in small, yellow prisms, m. p. 99°.

Anisaldehyde-p-ditolylhydrazone, $\text{N}(\text{C}_7\text{H}_7)_2 \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, forms large, flat needles, m. p. 126°.

Cuminaldehyde-p-ditolylhydrazone, $\text{N}(\text{C}_7\text{H}_7)_2 \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe}$, crystallises in long, silky needles, m. p. 104°.

Cinnamaldehyde-p-ditolylhydrazone, $\text{N}(\text{C}_7\text{H}_7)_2 \cdot \text{N} : \text{CH} : \text{CH} : \text{CHPh}$, forms flat, deep yellow needles, m. p. 143°.

Salicylaldehyde-p-ditolylhydrazone, $\text{N}(\text{C}_7\text{H}_7)_2 \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, is a greenish-yellow, crystalline powder, m. p. 126°.

Piperonaldehyde-p-ditolylhydrazone, $\text{N}(\text{C}_7\text{H}_7)_2 \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_3\text{O}_2 \cdot \text{CH}_3$, forms colourless leaflets, m. p. 134°. R. V. S.

Tetra-alkylation of 1-Methylcyclohexanone. ALBIN HALLES (*Compt. rend.*, 1913, 157, 179—185. Compare this vol., i, 629).—While the alkylation of cyclohexanone by means of sodamide proceeds but difficultly, methylcyclohexanone readily undergoes progressive alkylation. Thus 1-methylcyclohexan-6-one dissolved in ether, treated with sodamide, followed by the addition of methyl iodide, readily yields 1:5-dimethylcyclohexan-6-one, b. p. 170—171° (corr.), D_4^{20} 0.9146, n_D^{20} 1.4508 (compare Wallach, this vol., i, 482), together with a very small amount of the 1:1-isomeride. Further alkylation of the 1:5-compound yields 1:1:5-trimethylcyclohexan-6-one, b. p. 178—179°/755 mm. (corr.), D_4^{20} 0.9043, n_D^{20} 1.4493, yielding in its turn 1:1:5:5-tetramethylcyclohexan-6-one (*loc. cit.*). The corresponding alcohols are

obtained by reduction with sodium in absolute alcohol. 1:5-Dimethylcyclohexan-6-ol, a viscous liquid with an odour like eugenol, has b. p. 174.5—175.5°/748 mm. (corr.), D_4^{20} 0.9235, n_D^{20} 1.4628. 1:1:5-Tri-methylcyclohexan-6-ol has a similar odour, b. p. 186—187°/753 mm. (corr.), D_4^{20} 0.9128, n_D^{20} 1.4600.

Ethyl derivatives have been similarly prepared from 1-methylcyclohexan-6-one, the first stage giving 1-methyl-5-ethylcyclohexan-6-one, b. p. 194—196°/745 mm. (corr.), D_4^{20} 0.9162, n_D^{20} 1.4555. This then yields 1-methyl-1:5-diethylcyclohexan-6-one, b. p. 222—224°/757 mm. (corr.), D_4^{20} 0.9054, n_D^{20} 1.4572, and finally 1-methyl-1:5:5-triethylcyclohexan-6-one, b. p. 249—252°/765 mm. (corr.); b. p. 123—126°/16 mm. (corr.), D_4^{20} 0.9132, n_D^{20} 1.4634.

The corresponding alcohols have been prepared by reduction.

1-Methyl-5-ethylcyclohexan-6-ol, b. p. 202—204°/761 mm. (corr.), D_4^{20} 0.9268, n_D^{20} 1.4689.

1-Methyl-1:5-diethylcyclohexan-6-ol, b. p. 232—235°/749 mm. (corr.), D_4^{20} 0.9206, n_D^{20} 1.473.

1-Methyl-1:5:5-triethylcyclohexan-6-ol, b. p. 258—260°/759 mm. (corr.), D_4^{20} 0.9255, n_D^{20} 1.4769.

The successive introduction of methyl groups into cyclohexanone elevates the boiling point progressively, whilst causing a diminution in the density and the index of refraction, the same holding good for the corresponding alcohols.

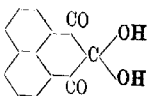
The introduction of ethyl groups into methylcyclohexan-6-one produces a steady rise in the boiling point, whilst the density diminishes for the first two stages and increases at the third, the refractive index showing steady rise throughout. The same remarks apply to the corresponding alcohols.

W. G.

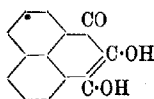
Interaction of Diketones and Acid Amides. L. H. FRIEDBURG (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 131).—When molecular quantities of pure benzil and benzamide are distilled, a quantitative yield of tizonitrile, together with benzaldehyde and benzoic acid, is obtained.

J. C. W.

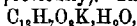
Oxidation of Hydroxyperinaphthindenone. III. GIORGIO ERRERA (*Gazzetta*, 1913, 43, i, 583—594. Compare Errera and Cuffaro, A., 1912, i, 273).—The paper deals with some derivatives of hydroxyperinaphthindenone obtained from a substance mentioned in a former paper (A., 1911, i, 465) as having been prepared by the action of phenylhydrazine on hydroxyperinaphthindenone. The constitution of this substance is still being investigated. It dissolves in bromine water, yielding the hydrate of perinaphthindantrione (annexed formula) (compare Ruhemann, T., 1911, 99, 1446), which forms golden-yellow, prismatic crystals. These begin to decompose at about 110°, yielding the anhydrous perinaphthindantrione, which forms red crystals, m. p. about 273° (decomp.). The hydrate dissolves in cold concentrated sodium carbonate, yielding a white, crystalline substance from which acids regenerate the triketone. The hydrate yields a sodium bisulphite



compound; hydroxylamine and phenylhydrazine do not give oxime or hydrazone, but reduce the substance. Both the hydrate and the anhydrous ketone readily yield an *alcoholate*, $C_{18}H_{12}O_4$, which crystallises in yellow, triclinic plates. The triketone reacts with *o*-phenylenediamine with production of the *phenazine*, $C_{18}H_{10}ON_2$, which crystallises in golden-yellow needles, m. p. 255—256°. The phenazine yields a *hydrazone*, $C_{25}H_{16}N_4$, crystallising in violet laminae, m. p. about 299° (decomp.).



Reduction of the triketone (best with phenylhydrazine) leads to the formation of *dihydroxyperinaphthindenone* (annexed formula), which can also be prepared by boiling the substance from phenylhydrazine and *hydroxyperinaphthindenone* with alcohol and sulphuric acid for six hours. *Dihydroxyperinaphthindenone* crystallises in silky, red needles, m. p. 258—259° (sintering previously). The *potassium salt*,



resembles permanganate in appearance. The salts of the substance are stable in the solid state, but are readily oxidised by air when in solution, yielding eventually naphthalic anhydride. Oxidation with bromine water regenerates the triketone. Conversely, the latter substance is partly reduced to *dihydroxyperinaphthindenone* when boiled with water. The author suggests that the blue coloration observed by Ruhemann (l., 1910, 97, 2027) when triketohydrindene is treated with potassium hydroxide is probably due to the transitory appearance of hydroxydiketohydrindene in its tautomeric form.

On esterification with methyl sulphate, *dihydroxyperinaphthindenone* yields a *monomethyl ether*, $C_{14}H_{10}O_8, H_2O$, crystallising in golden-yellow leaflets or needles, which on heating melt and lose water below 100°, giving the anhydrous substance, m. p. 115—135°. The *dimethyl ether*, $C_{15}H_{12}O_8$, is obtained by the same method, and forms golden-yellow needles, m. p. 84—85°. The *dibenzoyl derivative*, $C_{27}H_{16}O_8$, crystallises in greenish-yellow prisms, m. p. 217—218°. R. V. S.

Improved Method for the Production of β -Aminoanthraquinone. M. L. CROSSLEY (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 351—352).— β -Aminoanthraquinone has been obtained by Bourcart and also by Perger by heating sodium anthraquinone- β -sulphonate with solution of ammonia (25%) in a sealed glass tube. This method has now been found unsuitable for the preparation of the compound, as it is dangerous and gives only a small yield. A modified method has therefore been devised in which the reagents are heated at 150° in an iron tube, and the yield increased from 14% to 45%. When the ammoniacal filtrate from the β -aminoanthraquinone is acidified with hydrochloric acid, a brown precipitate is obtained which shows strong tinctorial properties with animal fibres. E. G.

Syntheses in the Terpene Group. WILLIAM H. PERKIN, jun. (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 224—264).—A review of the chemistry of the known and possible menthenols and menthadienes with special reference to the syntheses accomplished by Perkin and his collaborators. J. C. W.

Terpenes. Polymerisation of Pinene. GEORGE B. FRANKFORTER and F. W. POPPE (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 363—369).

—By the action of iodine on pinene in presence of aluminium iodide, a pinene *hydriodide*, b. p. 107°/7 mm., $D_{10} 1.447$, and $n_D 1.6245$, is produced, together with a *di-iodide*, $C_{10}H_{16}I_2$, b. p. 119—125°/7 mm., $D 1.69$. Both the hydriodide and di-iodide are decomposed by light with formation of dipinene and colophonene.

Dipinene, $(C_{10}H_{16})_2$, b. p. 172°/7 mm., $D_{10} 0.947$, $n_D^{20} 1.52517$, is optically inactive, and has a viscosity 101 at 25° as compared with water. *Colophonene*, $(C_{10}H_{16})_4$, m. p. 102—103°, is a pale yellow, crystalline substance; it yields two *tetrachloro-derivatives*, $(C_{10}H_{13}Cl)_4$, one, m. p. 119—121°, obtained by treating it with potassium permanganate and hydrochloric acid, and the other, m. p. 99—102°, obtained by the action of sulphuryl chloride. Both dipinene and colophonene are remarkably stable. E. G.

Constituents of Essential Oils. Reductions in the Sesquiterpene Group. FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber.*, 1913, 46, 2303—2308).—Eudesmene, b. p. 122—124°/7 mm., $D^{20} 0.91964$, $n_D 1.50874$, $[\alpha]_D +54.6^\circ$, obtained by the action of alcoholic potassium hydroxide on eudesmene dihydrochloride (which is produced when eudesmol is treated with hydrogen chloride in acetic acid solution; compare Semmler and Tobias, this vol., i, 885), can be reduced in acetic acid by free hydrogen under the catalytic influence of platinum black, producing *tetrahydroeudesmene*, $C_{15}H_{28}$, b. p. 122—122.5°/7.5 mm., $D^{20} 0.8893$, $n_D 1.48278$, $[\alpha]_D +10.2^\circ$.

Similar reduction of purified eudesmol, needles, m. p. 84°, not only removed the ethylenic linkings, but also affected the hydroxyl group, for the product is a *hydrocarbon*, $C_{15}H_{28}$, b. p. 117°/5.5 mm., $D^{20} 0.8896$, $n_D 1.48425$, $[\alpha]_D +11.8^\circ$; this is strikingly different from the result of reduction in ethereal solution (*loc. cit.*), the product of which is dihydroeudesmol, $C_{15}H_{28}O$.

The action of ozone on eudesmene in acetic acid solution gave decided indications of the distinct natures of eudesmene and selinene; one of the products was a *substance*, b. p. 180—200°/7 mm., $D^{20} 1.081$, $n_D 1.49429$, $[\alpha]_D +13^\circ$, which yields a *semicarbazone*.

Catalytic reduction of guajol, m. p. 91°, in acetic acid solution by free hydrogen resulted in the simultaneous elimination of the ethylenic linkings and the hydroxyl group with the formation of *tetrahydroguajene*, $C_{15}H_{28}$, b. p. 118—119°/7 mm., $D^{20} 0.8806$, $n_D 1.47840$, $[\alpha]_D +10.6^\circ$.

Reduction of tricyclic α -santalol, b. p. 147—148°/4.5 mm., $D^{20} 0.9745$, $n_D 1.50552$, $[\alpha]_D +0.6^\circ$, in a similar manner yielded almost quantitatively a bicyclic *tetrahydrosantalene*, $C_{15}H_{28}$, b. p. 115—116°/9 mm., $D^{20} 0.8655$, $n_D 1.46908$, $[\alpha]_D +5.6^\circ$, not only the ethylenic linkings and the hydroxyl group, but also one of the rings having been eliminated. Reduction of bicyclic β -santalol, b. p. 158—158.5°/5 mm., $D^{20} 0.97174$, $n_D 1.51357$, $[\alpha]_D -41.8^\circ$, yielded a product, b. p. 119°/10 mm., $D^{20} 0.8550$, $n_D 1.46612$, $[\alpha]_D +2.8^\circ$, which is mainly a *tetrahydrosantalene*, $C_{15}H_{28}$, probably containing a small quantity of a hexahydrosantalene due to a little monocyclic santalol, $C_{15}H_{24}O$, in the starting

product; at the same time in the reduction a bicyclic saturated alcohol, $C_{15}H_{26}O$, was obtained, b. p. $155-160/10$ mm., D^{20}_D 0.9380, n_D^{20} 1.4847, $[\alpha]_D +4.4^\circ$.
D. F. T.

The Essential Oil of Jamaica Ginger. FRANCIS D. DODGE (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 77-80).—The lowest-boiling fractions of oil of ginger contain an aldehyde, which may be removed as the bisulphite compound, and has now been identified with decaldehyde (compare von Soden, A., 1900, i, 605). The aldehyde has D^{16}_D 0.828, is optically inactive, is unstable towards alkalis, and changes spontaneously with the lapse of some years into an oil which smells like geraniol, and does not form a bisulphite compound or a semi-carbazone.
J. C. W.

Essential Oil of Witch Hazel. H. A. DICKINSON JOWETT and F. LEE PYMAN (*Pharm. J.*, 1913, 91, 129-130).—This oil had D 0.9001, an optical rotation of $+4.29^\circ$ in a 100 mm. tube, was slightly soluble in 90% alcohol, and gave a small quantity of colourless precipitate when mixed with absolute alcohol. It was found to consist chiefly of a sesquiterpene having D^{15}_D 0.8970, $n_D +14.88^\circ$, and n_D 1.4916. A trace of a phenolic substance, a mixture of fatty acids in the free and combined state, and a mixture of solid saturated hydrocarbons were also isolated, whilst indications of the presence of other compounds, including oxygenated substances, were obtained. The oil contained 0.6% of acids (expressed as acetic acid) and 7.3% of esters (expressed as $C_{10}H_{17}\cdot C_2H_5O_2$).
W. P. S.

Chemistry of Wood. The Resins of the Douglas Fir. GEORGE B. FRANKFORTER and HAROLD H. BROWN (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 359).—The resin extracted from the wood of the Douglas fir yields a crystalline acid, $C_{17}H_{24}O_2$, m. p. $143.5-144.5^\circ$, which has been termed *betic acid*; its salts, and bromine and iodine compounds have been prepared.
E. G.

Oxidation of Caoutchouc. FRANZ KIRCHHOF (*Kolloid. Zeitsch.*, 1913, 13, 49-61).—The author has carried out experiments on the oxidation of raw and vulcanised caoutchouc by means of air at the ordinary temperature and at 100° . It is shown that on account of the unsaturated nature of the caoutchouc, an autooxidation occurs which gives rise to the formation of a relatively unstable peroxide, which then undergoes a secondary oxidation: (1) $C_{10}H_{16} + O_2 \rightarrow C_{10}H_{16}O_2$; (2) $C_{10}H_{16} + C_{10}H_{16}O_2 \rightarrow 2C_{10}H_{16}O$; (3) $C_{10}H_{16}O + O_2 \rightarrow C_{10}H_{16}O_3$. This process is accompanied, in the case of raw caoutchouc, by a softening of the material, which is quite sticky at first and later becomes hard and has a glassy nature. The latter condition is due to the presence of the higher oxidation products. The oxidation of vulcanised caoutchouc is in the same way to be regarded as a primary formation of a peroxide which then decomposes, producing the same soft and sticky substance. Further oxidation produces the hard substances and free sulphuric acid. The action of the acid appears also to consist in an oxidation of the rubber, since the acid

is reduced to sulphur dioxide. In the oxidation at 100° , a separation of water occurs; this appears to be a result of the formation of sulphuric acid, since under the same conditions raw caoutchouc does not give rise to water.

It is further shown that the combined sulphur-content after oxidation and extraction with alkali is reduced to two-thirds of the amount originally contained in the product. This and other observations lead to the conclusion that vulcanisation consists in the addition of S_2 or of a thiozone molecule to the hydrocarbon residue. Since the thiozone molecule is unstable, it is likely that vulcanised caoutchouc is a thiozonide, which probably is transformed into other products in the ageing process, and since the formation of the thiozone occurs most readily at 135 – 160° , the part played by the vulcanisation catalysts is to be explained by a local raising of the temperature. In the oxidation of caoutchouc by air, a notable increase in weight occurs with the formation of products soluble respectively in acetone and alkali which have an acidic character. It is also indicated that the bromide and nitrosite methods for the analysis of rubber consist of oxidation processes which are probably responsible for the untrustworthy nature of the results of these processes.

J. F. S.

Synthesis of Glucosides by means of Ferments. ÉMILE BOURQUELOT (*Bull. Soc. chim.*, 1913, [iv], 13, i—xxviii).—A lecture delivered to the Chemical Society of France on May 9th, 1913.

J. F. S.

Synthetic β -Glucosides of Terpene Alcohols. III. JUHO HÄMÄLÄINEN (*Biochem. Zeitsch.*, 1913, 53, 423–428. Compare this vol., i, 497, 639, 888).—By condensation of α -santenol and camphene hydrate with bromoacetyldextrose in the presence of silver carbonate, and the subsequent hydrolysis of the acetyl derivatives, the glucosides were obtained. *α -Santenoltetra-acetyl-d-glucoside*, $C_{23}H_{34}O_{10}$, m. p. 135.5 – 137° (corr.), yields on hydrolysis *α -santenol-d-glucoside*, $C_{13}H_{20}O_6$, m. p. 122.5 – 125.5° (corr.), $[\alpha]_D^{20} - 44.63^{\circ}$. It is readily hydrolysed by emulsin.

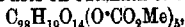
Camphenhydrate tetra-acetyl-d-glucoside, $C_{24}H_{36}O_{11}$, m. p. 115 – 117° (corr.), yields on hydrolysis *camphenhydrate-d-glucoside*, $C_{15}H_{28}O_6$, m. p. 96.5 – 102.5° (corr.), $[\alpha]_D^{20} - 30.56^{\circ}$, which is slowly hydrolysed by emulsin.

S. B. S.

Eutannin. WILHELM RICHTER (*Chem. Zentr.*, 1913, i, 1820–1821; from *Arb. Pharm. Inst. Univ. Berlin*, 9, 85–112).—Eutannin has the composition $C_{28}H_{24}O_{19} \cdot H_2O$, $[\alpha]_D^{25} + 58.9^{\circ}$, and forms a crystalline sodium salt. It contains a carboxyl group and a lactone or anhydride grouping. When heated in a stream of hydrogen at 240° , a molecule of carbon dioxide is eliminated and pyrogallol sublimes. Some diphenylmethane is formed on distillation with zinc dust. *Eutannin hydrate*, $C_{28}H_{26}O_{20}$, contains two carboxyl groups owing to the opening of the lactone or anhydride ring; the disodium salt forms a colourless precipitate. Eutannin is hydrolysed by emulsin to gallic acid and a substance which reduces Fehling's solution on boiling. Gallic acid is similarly formed on hydrolysing with 10% sulphuric acid.

Acetylcutannin, $C_{28}H_{15}O_9(CO \cdot CH_3)_{11}$, formed on boiling with acetic anhydride, is a colourless powder composed of tiny, crystalline splinters which sinter at $180-185^\circ$, decomp. 215° .

Methyl chloro-formate acts on eutannin to form a compound



a colourless, amorphous powder, which sinters at $150-153^\circ$, decomp. 180° . Diazomethane acting on this introduces four further methyl groups, yielding a product $C_{28}H_{15}O_{10}(O \cdot CO_2Me)_5(OMe)_4 \cdot H_2O$. This is composed of small, crystalline splinters, which sinter at 125° , m. p. 137° , decomp. 179° .

Diazomethane acting on eutannin produces at first the methyl derivative, $C_{28}H_{20}O_{15}(OMe)_4$, an amorphous powder, which sinters at 145° , decomp. $210-215^\circ$. On continued treatment the fully methylated compound, $C_{28}H_{15}O_{10}(OMe)_9$, is obtained, forming minute, crystalline splinters, m. p. $154-155^\circ$. On hydrolysis with sodium hydroxide, trimethylgallic acid is obtained.

The tannin obtained on hydrolysis of eutannin with sodium hydroxide has the composition $C_{14}H_{16}O_{11}$. Six hydroxyl groups in it are replaced by $-O \cdot CO_2Me$ on treatment with methyl chloro-formate. The formula $[(OH)_3C_6H_2 \cdot CO \cdot O]_2C_6H_2(CO_2H) \cdot O \cdot C_6H_4O(CO)(OH)_4$ is proposed for eutannin.

E. F. A.

Arsenites of Alkaloids. ALFRED C. MANGOLD (*Eighth Inter. Cong. App. Chem.*, 1912, 17, 37-43).—Analyses of compounds of arsenious acid with various alkaloids showed that the acid does not form true salts with quinine, cinchonidine, cinchonine, quinidine, brucine, and strychnine; the compounds obtained under varying conditions of preparation were mixtures of arsenious acid with the alkaloids. Arsenic acid, however, forms well-crystallised, definite salts with these alkaloids.

W. P. S.

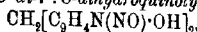
Occurrence of Histidine-betaine in Fungi. ERNST WINTERSTEIN and CAMILLE REUTER (*Zeitsch. physiol. Chem.*, 1913, 86, 234-237).—The base $C_9H_{15}O_2N_3$ obtained by Reuter (A., 1912, ii, 593) from fungi is shown to be histidine-betaine identical with that obtained by Barger and Ewins (this vol., i, 529) from ergothionin and the synthetic product made by Engeland and Kutscher (*ibid.*). The monoperate, m. p. 201° , forms slender, soft needles. The dipicrate, $2H_2O$, loses this water at 105° , and forms flat, thin prisms, or long plates, m. p. $212-213^\circ$. The base has $[\alpha]_D +41.1^\circ$.

E. F. A.

Some Derivatives of 8-Hydroxyquinoline. HANS SCHÜLLER (*J. pr. Chem.*, 1913, [ii], 88, 180-188).—8:8'-*Dihydroxy-5:5'-di-quinolylmethane*, $CH_2(C_9H_7N \cdot OH)_2$, obtained in the form of its sulphate (stellar aggregates of yellow needles, m. p. $198-200^\circ$) by the addition of 40% aqueous formaldehyde to a well cooled solution of 8-hydroxyquinoline in sulphuric acid, is precipitated from its salts by aqueous ammonia as a white, amorphous precipitate (decomp. 247°), which separates from pyridine in hexagonal crystals and couples with diazotised *m*-toluidine and α -naphthylamine, yielding carmine-red and reddish-brown *azo-dyes*. The *hydrochloride*, $B, 2HCl$, crystallises in

radiating clusters of lustrous, silky needles (decomp. 260°); the *zinc-chloride* forms yellowish-green, prismatic crystals; the *diacetyl* derivative has m. p. 160° , and decomposes slowly on exposure to air; the *libenzoyl* derivative, prepared by the pyridine method, separates from alcohol in small crystals, and has an odour resembling that of ethyl benzoate.

7:7'-Dinitroso-8:8'-dihydroxy-5:5'-diquinolylmethane (or 7:7'-dimimino-8:8'-diketo-5:5'-di-7:8-dihydroquinolylmethane),



or $\text{CH}_2(\text{C}_9\text{H}_4\text{ON}\cdot\text{N}\cdot\text{OH})_2$, prepared by the addition of sodium nitrite to an aqueous solution of the sulphate or hydrochloride, is a yellow crystalline substance, which explodes at about 130° , and is precipitated from its solution in sodium carbonate by acetic acid in a red, gelatinous condition. With salts of iron, nickel, copper, and many other metals, it yields coloured precipitates, which are more or less soluble in mineral acids, but insoluble in dilute acetic acid. Unsuccessful attempts to condense 8-hydroxyquinoline with oxalic acid, formic acid, and carbon tetrachloride are also recorded. F. B.

The Desmotropy of *o*- and *p*-Quinonoid Salts in the Thiazine Group. RUDOLF PUMMERER and SEBASTIAN GASSNER (*Ber.*, 1913, 46, 2310—2327).—In order to throw further light on the debated constitution of the thiazines, the authors have turned their attention to some of the simpler salts and have examined them chemically and optically; they find in certain cases an equilibrium between the ortho- and para-constitutions favoured by Kehrman and Hantzsch respectively.

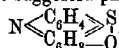
Their results with the phenazothionium salts differ in several respects from those of Kehrman and Veselý (*A.*, 1902, i, 186). The action of bromine on an alcoholic solution of thiodiphenylamine at even -15°

yielded a *dibromide*, $\text{NHBr} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{SBr}$, prisms, which readily decomposes with liberation of hydrogen bromide; it is reconverted by sulphurous acid into thiodiphenylamine. The *dichloride* is still less stable, but the more stable *di-iodide*, blackish-brown crystals, can be obtained by double decomposition of the dibromide and potassium iodide and also by the action of iodine on thiodiphenylamine in chloroform solution. Treatment of an acetone solution of the di-iodide with sodium acetate causes the production of a salt derived probably from a bimolecular colourless base.

The ferrochloride described earlier, from its quantitative reduction with stannous chloride, appears to be a *meri*-quinonoid compound which readily accounts for the deposition of thiodiphenylamine when its solution in hydrochloric acid is diluted. *Phenazothionium perchlorate*, obtained by the action of perchloric acid on diphenylaminesulphoxide (Barnett and Smiles, *T.*, 1910, 97, 186), is a stable, crystalline substance, which, like the phenazothionium salts generally, shows in dilute hydrochloric acid an absorption band in the green portion of the spectrum; a green *diperchlorate* was also obtained. In addition to the green picrate obtained by Kehrman and Veselý, the authors have isolated the unstable brown intermediate product, which proves to

be of the same composition, the green picrate being regarded as a polymeride of the brown; a very dilute solution of the green picrate in nitrobenzene turns brown, the change in colour being favoured by warming and dilution, whilst stronger solutions of both forms at first have the characteristic colour of the respective solids, but shortly assume an intermediate tone.

Phenazothione (for which the authors prefer the term thiazone), obtained by a slight modification of Kehrman's method, judging from its absorption spectrum and its reaction with magnesium phenyl bromide, can hardly have the suggested phenol-betaine structure:



This view is confirmed by the behaviour of its *hydrochloride*, which exists in two forms. On intimately mixing the base with hydrochloric acid a brown solution is obtained which changes to violet and subsequently deposits violet needles; the violet hydrochloride can be obtained directly by reaction in benzene-ether solution. The conversion of the brown form into the violet could be followed photometrically, and it was found that a unimolecular reaction occurs, yielding an equilibrium mixture, and that the velocity is independent of the concentration; from these facts the change must be an isomerisation, probably of the brown para-quinonoid salt, $\text{N} \begin{array}{c} \text{C}_6\text{H}_3\text{O}(\text{HCl}) \\ \text{C}_6\text{H}_4 \end{array} \text{S}$, into violet

ortho-quinonoid, $\text{N} \begin{array}{c} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_4 \end{array} \text{S} \cdot \text{HCl}$; reduction of the brown salt (which was only obtained in solution) was usually accompanied by more or less isomerisation to the violet salt, which is less easily reduced. Only one *hydriodide* was obtainable, and from its brown colour it is probably of the para-quinonoid structure. Similar phenomena are met with 3-methoxythiodiphenylamine, leaflets, m. p. 163°, which on oxidation by *p*-benzoquinone in acetic acid containing a little sulphuric acid gives a mixture of ortho- and para-quinonoid salts; addition of perchloric acid causes precipitation of the *o*-quinonoid violet *perchlorate*, which in the absence of any excess of acid gives a brown solution in water, but on addition of a few drops of acid the violet form is obtained. With 3-benzoyloxythiodiphenylamine, leaflets, m. p. 202–203°, obtained like the corresponding methoxy-compound by acting on a reduced solution of phenazothione, only ortho-quinonoid salt formation could be observed.

The acetylated amino-compounds, such as diacetylthionine (free base, needles, decomp. above 250°), are only ortho-quinonoid, whilst from similar colour considerations aminophenazothionium hydrochloride is of para-quinonoid constitution, but shows desmotropy analogous to that of phenazothione hydrochloride, and is transformed by concentrated acid into a brown ortho-quinonoid salt. Indications of such structural change could also be detected with thionine, but not with methylene-blue.

D. F. T.

The Deepening of Colour by Auxochrome Groups and Colours of an Higher Order. FRITZ STRAUS and A. ZEIME (*Ber.*, 1913, 46, 2267–2283).—From a study of the *meri*-quinonoid salts of

the *p*-phenylenediamine and benzidine series, Piccard (this vol., i, 895) has drawn the conclusion that Nietzki's rule, concerning the deepening of the colour from yellow to green by auxochrome groups, requires extension so as to include colours of a higher order. When the auxochromic effect has been gradually increased by substitution so that the colour has successively passed from yellow to red, blue and green, further increase in the auxochrome action is accompanied by a repetition of the colours in the same order; the colours of the second series are said to be of the second order.

The authors have arrived at the same conclusion from a consideration of the relationship of the yellow auramine to the blue and green dyes of the diaminodiphenyl and diaminotriphenyl series previously described by Straus and Bormann (A., 1910, i, 281). The latter dyes are derived from the reddish-blue salts of tetramethyldiaminobenzhydrol, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \cdot \text{Cl}$ (I), by replacement of the central methane hydrogen by chlorine, cyanogen, phenyl and other groups.

The yellow auramine and the orange-yellow salts of Michler's ketone differ from the above dyes in that the chromophoric groups are replaced by the auxochromic, hydroxyl and amino-groups, which thus cause a change in colour from blue to yellow; the yellow colour of the auramine is, therefore, considered to be of the second order.

This view is supported by the observation of Semper (A., 1911, i, 577), that the acetylated auramine base yields reddish-blue salts, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NHAc}) : \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \cdot \text{Cl}$; the auxochromic effect of the amino-group almost completely disappears on acetylation, so that the yellow colour of the second order of the auramine passes back again into the blue colour of the first order shown by the parent substance (I).

The conception of colours of a higher order also throws light on the relationships existing between the dyes of the diamino- and triamino-triphenyl series. The dyes of the triamino-series are not so deep in colour as those of the diamino-series, although they are produced from the latter by the introduction of the auxochrome amino-group. Thus, the red magenta corresponds with Döbner's violet, and the reddish-violet tetramethylmagenta with malachite-green. On the other hand, if the effect of the third amino-group in the magenta series is caused to disappear by acetylation, or by the conversion of the nitrogen atom into the quinquivalent condition, the colour apparently deepens. These anomalies disappear if it is assumed that the colours of the triaminotriphenyl series are of the second order, and those of the malachite-green group of the first order.

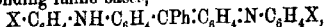
The authors also point out that whilst nitrosobenzene in the unimolecular condition is bluish-green and *p*-nitrosodimethylaniline pure green, the colour of *p*-nitrosodiphenylamine is yellow, and that tetramethyldiaminothiobenzophenone is orange-red, whilst thiobenzophenone is blue; from this the conclusion is drawn that the colours of *p*-nitrosodiphenylamine and tetramethyldiaminothiobenzophenone are of the second order.

Attempts have been made to prepare dyes having colours of the second order by replacing the *p*-hydrogen atoms of the terminal phenyl groups in viridine, $\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh} : \text{C}_6\text{H}_4 \cdot \text{NHCl} \cdot \text{C}_6\text{H}_5$, by chlorine,

bromine, methyl, methoxy- and ethoxy-groups. The attempts, however, were not successful, the various substituents producing very little change in the colour of the parent substance; even replacement of the terminal phenyl groups by the naphthyl or diphenyl groups failed to produce the desired effect.

The substituted viridines were all prepared by fusing di-*p*-methoxytriphenylcarbinol with the necessary substituted aniline (3 to 4 mols.) and benzoic acid (3 mols.) at 120–160° and isolated in the form of their chlorides.

The corresponding imine bases,



crystallise with benzene in dark reddish-brown needles having a green glance, and appear to polymerise when kept. The carbinols were prepared by dissolving the picrates or chlorides in pyridine and allowing the solution, after dilution with benzene or ether, to flow slowly into dilute aqueous alkali; only in a few cases could the carbinols be obtained crystalline. Ethers of the carbinols were also prepared, and resemble the latter in being difficult to obtain in the crystalline condition.

The chloride of di-*p*-methylviridine, prepared from *p*-toluidine, separates from acetone in small, lustrous, bronze crystals of the composition $C_{35}H_{29}N_2Cl \cdot C_3H_5O$ (decomp. 248–250°); it crystallises with alcohol in needles having a green metallic glance. The picrate forms dark green needles, m. p. 211°, with previous sintering at 205°; the imine base has m. p. 182°.

The chloride of di-*p*-chloroviridine, prepared from *p*-chloroaniline, forms lustrous, metallic green needles, m. p. about 285°, the picrate, prismatic crystals, having a golden-yellow or green metallic lustre, m. p. 243°, with previous sintering at 236°; the imine base crystallises in dark brown needles, m. p. 136°, when rapidly heated.

The chloride of di-*o*-chloroviridine has m. p. 191°; the picrate crystallises in leaflets of a coppery-red, metallic lustre, m. p. 148°; the imine base has m. p. 107°.

The chloride of di-*p*-bromoviridine forms a powder having a bronze lustre, m. p. indefinite (290–305°); the picrate crystallises from acetone in prismatic crystals of a golden-yellow, metallic glance, m. p. 253–257°; the imine base has m. p. 186–187°.

The chloride of di-*p*-methoxyviridine forms green, metallic, lustrous needles; the picrate forms green or golden-bronze, lustrous crystals, m. p. 205–208°; the imine base, m. p. 167°, crystallises with benzene (1 mol.).

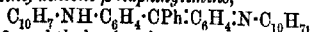
The chloride of di-*p*-ethoxyviridine has m. p. 243–245°; the picrate separates from acetone in light green, metallic, lustrous crystals, which on drying pass into a lustrous coppery modification, m. p. 176°; the imine base crystallises with benzene (1 mol.), m. p. 97°.

The following derivatives of di-*p*-nitroviridine were prepared: the chloride; picrate, lustrous, bronze crystals; imine base, dark brown needles, m. p. 176–178°; the carbinol, which sinters and decomposes at 110–115°, and is completely fused at 140°; the ethyl ether, which is light yellow, becomes brown at 200°, and has m. p. 204°.

The chloride of di-*p*-phenylviridine, prepared from *p*-aminodiphenyl,

forms a dark green, metallic, lustrous powder, m. p. 300—305°; the *picrate*, dark red scales, m. p. 252°, with previous sintering at 247°; the *imine base* crystallises with benzene (1 mol.), and has m. p. 136°; the *carbinol*, a light pink powder, and *ethyl ether* were also prepared.

β -Naphthylaminofuchsons- β -naphthylimine,



prepared from β -naphthylamine, has m. p. 147°; the *chloride* crystallises from acetone in brown needles of a bronze lustre, m. p. 290—300° (decomp.); the *picrate* in cubical crystals, sintering at 215°, m. p. 224°; the *carbinol* and *leuco*-compound do not crystallise.

F. B.

Ring Closing Accompanied by the Elimination of a Nitro-group from the Benzene Nucleus. SIEGMUND REICH and GEORGES GAIGALLIAN (*Ber.*, 1913, 46, 2380—2386).—When potassium hydroxide is added to 2:6-dinitrobenzaldehydophenylhydrazone, the red alcoholic solution becomes deep blue, but in a few minutes the colour lessens and changes to a pale yellow; pale yellow needles, m. p. 165°, crystallise out. The change is analogous to that observed by V. Meyer with the phenylhydrazones of methyl dinitrophenylglyoxylate (compare A., 1889, 516).

The blue colour is due to the formation of the potassium salt, $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{CH}\cdot\text{N}\cdot\text{NPhK}$, from which potassium nitrite is eliminated, and 7-nitro-1-phenylisindazole is formed, $\text{NO}_2\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CH} \\ \text{NPh} \end{smallmatrix}\text{N}$.

Corresponding isindazole derivatives are formed by the substituted phenylhydrazones, or by the naphthyl- or benzyl-hydrazones. The semicarbazone does not react in this manner.

When the imide hydrogen atom is replaced there is no reaction; thus neither the phenylmethyl- nor the phenylbenzyl-hydrazones shows the reaction.

The isindazole derivatives crystallise well, and are stable compounds. The presence of the phenyl and nitro-groups reduces the basic properties, so that the hydrochlorides are not precipitated on passing hydrogen chloride into the ethereal solution of the base. They are especially resistant towards reducing agents.

7-Nitro-1-phenylisindazole crystallises in yellow needles, m. p. 165°.

2:6-Dinitrobenzaldehyde-*p*-bromophenylhydrazone forms red crystals, m. p. 176° (blackening). The corresponding 7-nitro-1-*p*-bromophenylisindazole separates in yellow crystals, m. p. 183° (blackening).

2:6-Dinitrobenzaldehyde-*p*-nitrophenylhydrazone forms reddish-brown crystals, m. p. 207—208°. The isomeric *o*-nitrophenylhydrazone gives similar coloured crystals, m. p. 220—221°.

7-Nitro-1-*p*-nitrophenylisindazole yields yellow, microscopic crystals, m. p. 261°.

7-Nitro-1-*o*-nitrophenylisindazole forms yellow needles, m. p. 162—163°.

2:6-Dinitrobenzaldehyde- α -naphthylhydrazone forms red crystals, m. p. 205—206°.

7-Nitro-1- α -naphthylisindazole gives yellow crystals, m. p. 113—114°.

The isomeric β -naphthylhydrazones crystallises in tiny red needles, m. p. 183—184°, whilst the 1-nitro-1- β -naphthylisindazole separates in yellow crystals, m. p. 152—153°.

2:6-Dinitrobenzaldehydebenzylhydrazones crystallises in citron-yellow needles, m. p. 86°.

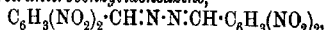
7-Nitro-1-benzylisindazole forms tiny, pale yellow, lustrous needles, m. p. 97—98°.

2:6-Dinitrobenzaldehydophenylmethylhydrazones separates in reddish-yellow crystals, m. p. 127°.

2:6-Dinitrobenzaldehydophenylbenzylhydrazones crystallises in yellow needles, m. p. 110°.

2:6-Dinitrobenzaldehydesemicarbazones forms a yellow, crystalline powder, m. p. 207—208°.

2:6:2':6'-Tetranitrobenzylideneazine,



prepared by the interaction of hydrazine hydrochloride with the aldehyde, forms pale yellow-coloured needles, m. p. 246—247°.

E. F. A.

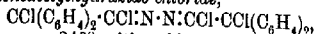
Bisdiphenyleneacetylhydrazide Chloride and its Reaction Products. ROBERT STOLLÉ, H. MÜNDEL, and F. WOLF (*Ber.*, 1913, 46, 2339—2352).—The elimination of halogen or of halogen hydracid at the 1:6-position occurs with bisdiphenyleneacetylhydrazide chloride just as with bisdiphenylacetylhydrazide chloride (Stollé and Laux, A., 1911, i, 508; Stollé and Schmidt, A., 1912, i, 980, 1035). Corresponding with the greater mobility of the α -hydrogen atom of diphenyleneacetic acid it is found that derivatives such as bisdiphenyleneacetylhydrazide chloride readily undergo oxidation to azo-compounds, whilst others can be further oxidised to tetrazine derivatives (compare Wislicenus and Russ, A., 1910, i, 840).

Diphenyleneacetylhydrazide, $\text{CH}(\text{C}_6\text{H}_5)_2\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, needles, m. p. above 360° (decomp.), was obtained by heating ethyl diphenyleneacetate with a sesquimolecular proportion of hydrazine hydrate at 120° for three hours; its *hydrochloride*, lustrous scales, is precipitated from solution by concentrated hydrochloric acid; *benzylidene* derivative, needles which sinter near 250°; *acetone* condensation product, lustrous needles, m. p. near 200° if rapidly heated.

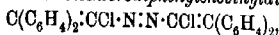
If diphenyleneacetylhydrazide is heated for two hours with ethyl diphenyleneacetate in molecular proportion at 250°, symmetrical *bisdiphenyleneacetylhydrazide*, $\text{CH}(\text{C}_6\text{H}_5)_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{C}_6\text{H}_5)_2$, needles, m. p. 340°, from nitrobenzene, is obtained, and it can also be produced by the interaction of equimolecular proportions of diphenyleneacetyl chloride and hydrazine hydrate in cooled ethereal solution. When treated in suspension in benzene or carbon tetrachloride with phosphorus pentachloride at water-bath temperature, this symmetrical hydrazide is converted into *bisdiphenyleneacetylhydrazide chloride*, $\text{CH}(\text{C}_6\text{H}_5)_2\cdot\text{CCl}\cdot\text{N}\cdot\text{N}\cdot\text{CCl}\cdot\text{CH}(\text{C}_6\text{H}_5)_2$, colourless crystals, which at its m. p. (approximately 192°) or in solution in boiling xylene or nitrobenzene assumes a deep red colour, due doubtless to elimination of hydrogen atoms at the 1:6-positions by oxidation with formation of the *azo*-compound, $\text{C}(\text{C}_6\text{H}_5)_2\cdot\text{CCl}\cdot\text{N}\cdot\text{N}\cdot\text{CCl}\cdot\text{C}(\text{C}_6\text{H}_5)_2$. The hydrazide

chloride, when treated in benzene solution with an alcoholic solution of sodium ethoxide or with ammonia, or such bases as mercuric oxide and lead oxide, loses a molecule of hydrogen chloride, producing *bisdiphenylenesuccinonitrile*, a colourless, crystalline powder, m. p. 242°. If in the reaction with sodium ethoxide the solution of the latter is a concentrated one and the reaction mixture is heated, the nitrile undergoes further hydrolysis with scission of carbon dioxide, yielding bisdiphenylene-ethane. By boiling with acetic acid and zinc dust the nitrile undergoes successive reduction and hydrolysis to diphenylene-acetamide, m. p. 251°.

If an intimate mixture of bisdiphenyleneacetylhydrazide chloride and phosphorus pentachloride is heated for an hour at 180—200°, *bischlorodiphenyleneacetylhydrazide chloride*,

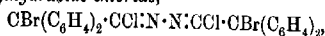


pale red crystals, m. p. 240°, with reddening, is obtained. When heated in high-boiling solvents, a deep red colour develops, due to elimination of chlorine and formation of *bischlorodiphenylenevinyl-di-imide*,



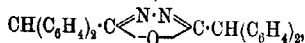
almost black, lustrous needles, m. p. 295°, which is best produced by the action of mercury on the bischlorodiphenyleneacetylhydrazide chloride in benzene solution; the di-imide can unite with chlorine regenerating its parent substance, and is further reduced in benzene solution by hydrazine hydrate, yielding 3:6-difluorenyldihydropyridazine,

$\text{CH}(\text{C}_6\text{H}_4)_2\cdot\text{C}\begin{smallmatrix} \text{N} \\ \text{NH}\cdot\text{NH} \end{smallmatrix}\text{C}\cdot\text{CH}(\text{C}_6\text{H}_4)_2$, m. p. 290°, and by acetic acid and zinc dust to iminomethylfluorene, m. p. 148—149° (compare Wislicenus and Russ, *loc. cit.*). The addition of bromine to bischlorodiphenylenevinyl-di-imide, effected in benzene solution, yields *bisbromodiphenyleneacetylhydrazide chloride*,

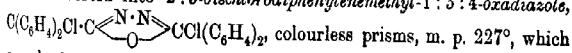


colourless crystals, m. p. 245°, which like the corresponding chloro-compound readily passes into the red azo-compound at its m. p. or when heated in high-boiling solvents. On treatment of the di-imide compound in benzene solution with amyl nitrite and acetic acid, the colour disappears and *α-nitroso-α'-hydroxy-αα'-bisdiphenyleneacetylhydrazide chloride*, $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4)_2\cdot\text{CCl}\cdot\text{N}\cdot\text{N}\cdot\text{CCl}\cdot\text{C}(\text{C}_6\text{H}_4)_2\cdot\text{NO}$, colourless, microscopic needles, m. p. near 145°, with reddening, is formed.

When bisdiphenyleneacetylhydrazide chloride is heated for several days in benzene solution with phosphoryl chloride and phosphoric oxide, *bisfluorenyl-1:3:4-oxadiazole*,

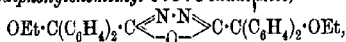


colourless needles, m. p. 223°, is obtained; this assumes a blue coloration at its m. p. or when heated in high-boiling solvents; by heating in benzene solution with phosphorus pentachloride for several hours it is converted into 2:5-bischlorodiphenylenemethyl-1:3:4-oxadiazole,



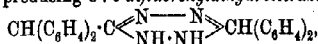
colourless prisms, m. p. 227°, which can also be obtained by the action of thionyl chloride on *α*-diphenyleneacetylhydrazide. This product when heated in high-boiling solvents, or

preferably when shaken in benzene solution with mercury, loses chlorine with formation of blue 2:5-bisdiphenylenemethylenedihydro-1:3:4-oxa-diazole, $C(C_6H_4)_2 \cdot C \begin{smallmatrix} \text{N} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} > C \cdot C(C_6H_4)_2$, m. p. above 360° , and when boiled in alcoholic solution for several days undergoes conversion into 2:5-bisethoxydiphenylenemethyl-1:3:4-oxadiazole,



a colourless, crystalline powder, m. p. 290° (decomp.).

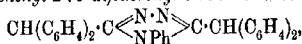
Bisdiphenyleneacetylhydrazide chloride, when heated under reflux for five hours with an equal quantity of hydrazine hydrate, condenses with the latter, producing 3:6-difluorenyldihydrotetrazine,



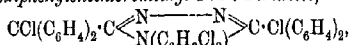
a colourless powder, m. p. 290° , together with 1-amino-2:5-difluorenyl-

1:3:4-triazole, $CH(C_6H_4)_2 \cdot C \begin{smallmatrix} \text{N} \text{---} \text{N} \\ \diagup \quad \diagdown \\ \text{N}(\text{NH}_2) \end{smallmatrix} > C \cdot CH(C_6H_4)_2$, microscopic tablets, m. p. 285° , which is also obtained by the action of hot alcoholic hydrogen chloride on the former product. The latter substance when treated in cold alcoholic solution with hydrogen chloride and sodium nitrite undergoes conversion into 2:5-difluorenyl-1:3:4-triazole, $CH(C_6H_4)_2 \cdot C \begin{smallmatrix} \text{N} \text{---} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} > C \cdot CH(C_6H_4)_2$, needles, m. p. 217° . The

interaction of bisdiphenylacetylhydrazide chloride and aniline at 150° gives rise to 1-phenyl-2:5-difluorenyl-1:3:4-triazole,



a pale yellow, crystalline powder, m. p. 270° , the course of the reaction being strikingly different from that with ammonia (see above). The last product, in suspension in carbon tetrachloride and exposed to the rays from a quartz lamp, is converted by chlorine into 1-dichloro-phenyl-2:5-bisdiphenylenechloromethyl-1:3:4-triazole,



a colourless powder, m. p. above 360° , the solution of which in molten naphthalene becomes blue on shaking with mercury, probably due to the formation of unstable 1-dichlorophenyl-2:5-bisdiphenylenemethylene-2:5-

dihydro-1:3:4-triazole, $C(C_6H_4)_2 \cdot C \begin{smallmatrix} \text{N} \text{---} \text{N} \\ \diagup \quad \diagdown \\ \text{N}(C_6H_4Cl_2) \end{smallmatrix} > C \cdot C(C_6H_4)_2$.

When shaken in benzene suspension with amyl nitrite, 3:6-difluorenyldihydrotetrazine becomes oxidised to 3:6-difluorenyltetrazine,

$CH(C_6H_4)_2 \cdot C \begin{smallmatrix} \text{N} \text{---} \text{N} \\ \diagup \quad \diagdown \\ \text{N}=\text{N} \end{smallmatrix} > C \cdot CH(C_6H_4)_2$, red needles, m. p. 225° (decomp.),

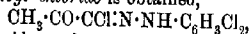
the reverse change being possible by reduction with zinc dust and acetic acid. 3:6-Difluorenyltetrazine when subjected to the action of chlorine in boiling carbon tetrachloride under the influence of rays from a quartz lamp gives 3:6-bischlorodiphenylenemethyltetrazine,

$CCl(C_6H_4)_2 \cdot C \begin{smallmatrix} \text{N} \text{---} \text{N} \\ \diagup \quad \diagdown \\ \text{N}=\text{N} \end{smallmatrix} > C(C_6H_4)_2Cl$, violet-black needles, m. p. 206° (decomp.), as a substitution product. Although already formed 3:6-

difluorenyltetrazine is not further oxidisable by amyl nitrite, if 3:6-difluorenyldihydratotetrazine is heated in benzene solution with amyl nitrite, the oxidation passes this stage, yielding 3:6-bisdiphenylenemethylenedihydratotetrazine, $C(C_6H_5)_2 \cdot C \begin{smallmatrix} \text{N}=\text{N} \\ \text{N}=\text{N} \end{smallmatrix} > C \cdot C(C_6H_5)_2$, green prisms, m. p. 240° (decomp.), which is also obtainable by the action of mercury on a benzene solution of 3:6-bischlorodiphenylenemethyltetrazine or 3:6-bisbromodiphenylenemethyltetrazine, into which substances it can be reconverted by the action of the respective halogens. When heated alone to 240° , 3:6-bisdiphenylenemethylenedihydratotetrazine loses half its total nitrogen, and passes into bisdiphenylenesuccinonitrile; by the action of bromine in benzene solution it is quantitatively converted into 3:6-bisbromodiphenylenemethyltetrazine, $CBr(C_6H_5)_2 \cdot C \begin{smallmatrix} \text{N}-\text{N} \\ \text{N}=\text{N} \end{smallmatrix} > C \cdot CBr(C_6H_5)_2$, a reddish-violet powder, decomp. near 260° , from which the bromine is removable by the action of mercury on its benzene solution. The action of sodium ethoxide on the bromine compound failed to yield any corresponding ethoxy-derivative, the only product being bisdiphenylene-ethane.

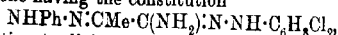
D. F. T.

Preparation and Reactions of 2:4-Dichlorophenylhydrazonopyruvyl Chloride. CARL BÜLOW and PETER NEBER (*Ber.*, 1913, 46, 2370—2379. Compare Bülow and Neber, this vol., i, 207).—On hydrolysing ethyl anilinoacetoacetate to the free carboxylic acid and allowing chlorine to act on this in alcoholic solution, 2:4-dichlorophenylhydrazonopyruvyl chloride is obtained,



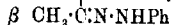
whereas carbon dioxide and hydrogen chloride are liberated. The chloride is very reactive; on treatment with ammonia or hydrazine, action can be controlled, so that only the chlorine and not the keto-group is replaced by the amino- or hydrazino-group with the formation of the basic compounds, (A) 2:4-dichlorophenylhydrazonopyruvamide, $CH_3 \cdot CO \cdot C(NH_2) : N \cdot NH \cdot C_6H_3Cl_2$, and (B) 2:4-dichlorophenylhydrazonopyruvylhydrazide, $CH_3 \cdot CO \cdot C \begin{smallmatrix} \text{NH} \cdot \text{NH}_2 \\ \text{N} \cdot \text{NH} \cdot C_6H_3Cl_2 \end{smallmatrix}$.

When phenylhydrazine acts on the aminohydrazone (A), the colourless basic osazone having the constitution

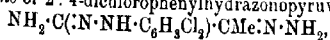


which is sensitive to light, is formed. The Bordeaux-red solution in concentrated sulphuric acid is turned blue both by oxidising agents and by atmospheric oxygen with the formation of osotetrazone.

The same osazone is obtainable from 2:4-dichlorophenylhydrazonopyruvyl chloride and phenylhydrazine, which condense to the phenylhydrazone of the chloride, $\alpha \quad ClC : N \cdot NH \cdot C_6H_3Cl_2$. This is



converted by alcoholic acid into the corresponding α -amino-osazone, The hydrazone of 2:4-dichlorophenylhydrazonopyruvamide,



is typical of another class of compounds belonging to the basic osazonoid series; it no longer dissolves with a characteristic coloration in concentrated sulphuric acid, and cannot be oxidised to osotetrazone. The corresponding *hydrazide* behaves similarly.

2:4-Dichlorophenylhydrazonopyruvyl chloride crystallises in snow-white needles, m. p. 125°, dissolving in concentrated sulphuric acid with a pure yellow coloration. With pyridine on boiling or on prolonged contact in the cold it forms a compound crystallising in red needles, m. p. 168°. The corresponding *amide* crystallises in centimetre-long, faintly yellow needles, m. p. 193°, and dissolves in concentrated sulphuric acid with a faint yellow coloration.

The *phenylhydrazone* of 2:4-dichlorophenylhydrazonopyruvamide separates in bunches of snow-white needles, m. p. 149° (decomp.).

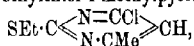
The *phenylhydrazones* of the corresponding *chloride* is deposited in large, straw-yellow needles from chloroform or fine matted needles from acetic acid, m. p. 208° (decomp.), giving a brownish-yellow solution in concentrated sulphuric acid.

The *hydrazone* of 2:4-dichlorophenylhydrazonopyruvamide crystallises in large, colourless needles becoming yellow on exposure; it sinters at 120°, m. p. 130°. The corresponding *acetylhydrazone* forms colourless crystals, m. p. 217°.

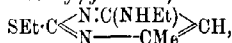
2:4-Dichlorophenylhydrazonopyruvylhydrazide forms pale yellow needles, m. p. 131°. It is remarkably electric. It dissolves in concentrated sulphuric acid with a yellowish-brown coloration which deepens on keeping. The corresponding *acetylhydrazide* crystallises in colourless needles which sinter at 150°, m. p. 199°; they become yellow on exposure.

E. F. A.

Purines. XI. 2:8-Dioxy-6-methyl-9-ethylpurine. CARL O. JOHNS and EMIL J. BAUMANN (*J. Biol. Chem.*, 1913, 15, 119—125).—The preparation of a derivative of 9-ethylpurine is described. 6-Chloro-2-ethylthiol-4-methylpyrimidine,



was heated with aqueous ethylamine, and gave an excellent yield of 6-ethylamino-2-ethylthiol-4-methylpyrimidine,



colourless, pointed prisms, m. p. 70°. Boiling with hydrochloric acid converted this into 6-ethylamino-4-methyl-2:3-dihydro-2-pyrimidone, $\text{CO} \begin{array}{c} \text{N} \cdot \text{C}(\text{NEt}) \\ \text{NH} \text{---} \text{CMe} \end{array} \text{CH}$, acicular prisms, m. p. 245—250° (decomp.)

(hydrochloride, colourless, diamond-shaped plates, m. p. 214—215°); this gave 5-nitro-6-ethylamino-4-methyl-2:3-dihydro-2-pyrimidone, colourless needles, decomp. 238°, charring at 260—265°, which was very readily reduced by means of freshly precipitated ferrous hydroxide to 5-amino-6-ethylamino-4-methyl-2:3-dihydro-2-pyrimidone,

$\text{CO} \begin{array}{c} \text{N} \cdot \text{C}(\text{NEt}) \\ \text{NH} \text{---} \text{CMe} \end{array} \text{C} \cdot \text{NH}_2$, clusters of needles. Heating with carb-

amide converted this into the desired 2:8-dioxy-6-methyl-9-ethylpurine,

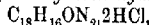
$\text{CO} \begin{array}{c} \text{N:CMe} \\ \text{NH} \end{array} \text{C} \begin{array}{c} \text{NH} \\ \text{NEt} \end{array} \text{CO}$, which crystallises in sheaves of needles like tyrosine; it has a pearly lustre, and does not melt at 310° .

E. F. A.

Etherification of *o*-Hydroxyazo-compounds. III. G. CHARRIER and G. FERRERI (*Atti R. Accad. Sci. Torino*, 1913, 48, 854—872. Compare A., 1912, i, 812; this vol., i, 535).—In the present paper are described nitrates of azo-2-naphthyl ethers. They are obtained by adding an ethereal solution of nitric acid to ethereal solutions of the ethers. They are more stable than the corresponding hydrochlorides (*loc. cit.*), and have a definite m. p., but on cooling after fusion an equimolecular mixture of the corresponding 1-nitro-2-naphthyl ether and the diazonium nitrate is found to have been formed. The constitution of these nitrates is probably that represented by the formula: $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N:NHAr(ONO}_2\text{)} \\ \text{OHR(ONO}_2\text{)} \end{array}$.

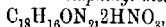
The nitrate of 1-benzeneazo-2-naphthyl methyl ether, m. p. 67° , has already been described (*loc. cit.*), as has also the corresponding ethyl ether derivative, m. p. $80-81^{\circ}$.

1-*o*-Tolueneazo-2-naphthyl methyl ether hydrochloride,



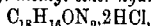
forms metallic green needles; the nitrate, $\text{C}_{15}\text{H}_{15}\text{ON}_2 \cdot 2\text{HNO}_3$, forms large, green, acicular crystals, m. p. 71° (decomp.). The nitrate of the ethyl ether, $\text{C}_{19}\text{H}_{19}\text{ON}_2 \cdot 2\text{HNO}_3$, crystallises in cantharides-green laminae, m. p. $62-63^{\circ}$ (decomp.).

The nitrate of 1-*m*-tolueneazo-2-naphthyl methyl ether,

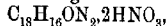


forms cantharides-green leaflets, m. p. 72° (decomp.). The nitrate of the ethyl ether, $\text{C}_{18}\text{H}_{18}\text{ON}_2 \cdot 2\text{HNO}_3$, m. p. 84° (decomp.), crystallises similarly.

1-*p*-Tolueneazo-2-naphthyl methyl ether hydrochloride,



crystallises in red needles having a golden lustre. The hydrobromide, $\text{C}_{18}\text{H}_{16}\text{ON}_2 \cdot 2\text{HBr}$, forms metallic green needles. The nitrate,



m. p. 77° (decomp.), forms dark red needles with a green metallic lustre. The nitrates of the ethyl ether, $\text{C}_{19}\text{H}_{18}\text{ON}_2 \cdot 2\text{HNO}_3$, m. p. 94° (decomp.), crystallises in garnet-red leaflets, which have a golden lustre.

1-*o*-4-Xyleneazo-2-naphthol, $\text{C}_{15}\text{H}_{16}\text{ON}_2$, crystallises in cherry-red needles with a golden lustre, and has m. p. 146° ; it dissolves in concentrated sulphuric acid, giving an intense red coloration. The methyl ether, $\text{C}_{19}\text{H}_{18}\text{ON}_2$, forms red, prismatic leaflets, m. p. 106° . The hydrochloride of the methyl ether, $\text{C}_{19}\text{H}_{18}\text{ON}_2 \cdot 2\text{HCl}$, forms red needles having a golden lustre. The hydrobromide, $\text{C}_{19}\text{H}_{18}\text{ON}_2 \cdot 2\text{HBr}$, crystallises in garnet-red needles. The nitrate, $\text{C}_{19}\text{H}_{18}\text{ON}_2 \cdot 2\text{HNO}_3$, m. p. $87-88^{\circ}$ (decomp.), crystallises in coffee-coloured scales, which have a golden lustre. The ethyl ether, $\text{C}_{20}\text{H}_{20}\text{ON}_2$, m. p. $94-95^{\circ}$, forms

red needles which have a golden lustre. The *hydrochloride* of the ethyl ether, $C_{20}H_{20}ON_2 \cdot 2HCl$, crystallises in metallic, coffee-coloured needles. The *hydrobromide*, $C_{20}H_{20}ON_2 \cdot 2HBr$, forms red needles.

1-m-4-*Xyleneazo-2-naphthyl methyl ether*, $C_{19}H_{18}ON_2$, m. p. $72-73^\circ$, crystallises in garnet-red, prismatic leaflets, which have a violet lustre. The *hydrochloride*, $C_{19}H_{18}ON_2 \cdot 2HCl$, and the *hydrobromide*,

$C_{19}H_{18}ON_2 \cdot 2HBr$, crystallise in microscopic, red needles. The *nitrate*, $C_{19}H_{18}ON_2 \cdot 2HNO_3$, forms cantharides-green needles, m. p. 83° (decomp.). 1-m-4-*Xyleneazo-2-naphthylamine*, $C_{18}H_{17}N_3$, crystallises in orange-red leaflets, m. p. 128° ; it dissolves in concentrated sulphuric acid, giving a reddish-violet coloration. 1-m-4-*Xyleneazo-2-naphthyl ethyl ether*, $C_{20}H_{20}ON_2$, forms garnet-coloured needles, m. p. 47° . The *hydrochloride*,

$C_{20}H_{20}ON_2 \cdot 2HCl$, forms coffee-coloured needles, and the *hydrobromide*, $C_{20}H_{20}ON_2 \cdot 2HBr$, crystallises in garnet-red needles. The *nitrate*, $C_{20}H_{20}ON_2 \cdot 2HNO_3$, forms cantharides-green needles, m. p. 82° .

1-p-*Xyleneazo-2-naphthyl methyl ether*, $C_{19}H_{18}ON_2$, crystallises in garnet-red, prismatic tablets, m. p. $91-92^\circ$. The *hydrochloride*, $C_{19}H_{18}ON_2 \cdot 2HCl$, forms garnet-red needles, and the *hydrobromide*, $C_{19}H_{18}ON_2 \cdot 2HBr$, forms coffee-coloured needles. The *nitrate*,

$C_{19}H_{18}ON_2 \cdot 2HNO_3$, crystallises in cantharides-green laminae, m. p. 75° (decomp.). The *ethyl ether*, $C_{20}H_{20}ON_2$, crystallises in aggregates of red laminae, or in needles, m. p. $61-62^\circ$. The *hydrochloride*, $C_{20}H_{20}ON_2 \cdot 2HCl$, forms copper-coloured needles, as does also the *hydrobromide*,

$C_{20}H_{20}ON_2 \cdot 2HBr$. The *nitrate*, $C_{20}H_{20}ON_2 \cdot 2HNO_3$, forms dark red, prismatic laminae, m. p. 71° (decomp.).

The *hydrochloride* of 1- α -naphthaleneazo-2-naphthyl methyl ether, $C_{21}H_{16}ON_2 \cdot 2HCl$, crystallises in bluish-violet needles, and the *hydrobromide*, $C_{21}H_{16}ON_2 \cdot 2HBr$, forms iridescent, greenish-brown needles.

R. V. S.

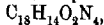
Formation of the Azo- and Bisazo-phenols. GIACOMO PONZIO (*Gazzetta*, 1913, 43, i, 559-562).—Azo- and bisazo-phenols can be prepared very conveniently by keeping benzenediazonium acetate for a short time. If the solution prepared by diazotising 9.3 grams of aniline in the presence of 20 c.c. of hydrochloric acid (D 1.19) is treated with 25 grams of sodium acetate and diluted to a volume of 5 litres, *p*-benzeneazophenol is deposited after keeping for twenty-four hours at the ordinary temperature. The substance forms yellow leaflets, m. p. 154° , although in the literature the m. p. 148° is usually given. Both its acetate and its benzoate exhibit chromoisomerism, for they exist in red and in yellow forms. If phenol is added to the above solution an immediate precipitate of the azo-compound occurs, so that its spontaneous production when the solution is kept is due to interaction of the diazo-compound with phenol which is slowly formed from it.

If the above-mentioned solution is diluted to a volume of only

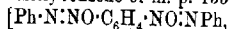
500 c.c., 2:4-bisbenzeneazophenol is rapidly deposited by it. In the same way, the corresponding bisazocresol, as well as the azocresol, can be obtained from *o*-toluidine.

R. V. S.

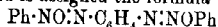
Polyazoxy-compounds. II. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 844—850. Compare this vol., i, 658).—The present paper deals with bisazoxybenzene, previously described (*loc. cit.*). On reduction with aluminium amalgam it yields bisazobenzene (Mills, T., 1895, 67, 929). By the action of concentrated sulphuric acid at 100°, bisazoxybenzene yields benzeneazobenzeneazophenol (*loc. cit.*), which is identical with that obtained by diazotising aminoazobenzene and treating the product with phenol. This derivative yields an *ethyl ether*, $C_{20}H_{18}ON_4$, which crystallises in red laminae, melting to a turbid liquid at 138°, becoming then viscous and subsequently limpid again at about 210°. When bisazoxybenzene is treated with concentrated sulphuric acid for some hours at 0°, three substances are formed: (1) a substance, $C_{18}H_{14}O_2N_4$, which forms ruby-red crystals, m. p. 203°; (2) a substance, $C_{18}H_{14}O_2N_4$, which crystallises in shining, orange-yellow laminae, m. p. 168°; and (3) a substance,



crystallising in deep orange-yellow laminae, m. p. 148°. The first-mentioned compound (m. p. 203°) is soluble in alkalis and yields a *benzoyl* derivative, $C_{25}H_{18}O_2N_4$ (yellow crystals, m. p. 178°) and an *ethyl* derivative, $C_{20}H_{18}O_2N_4$ (orange-coloured prisms, m. p. 142°, forming a turbid liquid which becomes clear about 180°). The compound of m. p. 168° yields bisazobenzene on reduction, and gives a small quantity of a polybromo-derivative when heated with bromine; it is an isomeride of the bisazoxybenzene of m. p. 155°



termed the β -form], and is assigned the formula



(α -form). The compound of m. p. 148° is probably a third isomeride (γ -form), to which the constitution $Ph \cdot NO : N \cdot C_6H_4 \cdot NO : NPh$ is ascribed.

R. V. S.

Colloidal Chemical Studies on the Proteins. HUGO ROHONYI (*Biochem. Zeitsch.*, 1913, 53, 179—209).—Solutions of proteoclastic ferments possess the property of precipitating proteins and albumoses from their solutions under certain conditions. The latter are as follows: (1) The solutions should contain at the most only traces of neutral salts, as the precipitates are soluble in salt solutions; (2) as the precipitates are soluble in acids and alkalis, precipitation only takes place within narrow limits of the hydrogen-ion concentration; (3) the reacting substances must be present in certain definite proportions, as the precipitates are often soluble in excess of either reagent. The reactions can take place even after activation of the ferment, and the precipitates are probably complexes of the protein and ferment. If acid is added to protein solutions, and the conductivity curve is plotted, the formation of precipitates causes no discontinuity in the curve. The combination of acids with proteins depends there-

fore on the absolute amount of protein present, and is independent of the surface of the latter. Paranuclcin is not a product of hydrolysis, but a caseinogen-caseose complex. The paranuclcin of Brailford Robertson is a complex compound of caseose and a protein contained in Grüber's pepsin preparation. It is not formed when certain other preparations of pepsin are employed. Reasons are given for supposing that the so-called plasteins are complex albumose-enzyme compounds.

S. B. S.

The Precipitation of Egg-Albumin by Ammonium Sulphate. The Theory of the "Salting Out" of Proteins. HARRIETTE CHICK and CHARLES J. MARTIN (*Biochem. J.*, 1913, 7, 380—398).—The precipitation of egg-albumin by ammonium sulphate is, as Spiro showed for sodium sulphate and caseinogen and gelatin, due to the separation of the system into a protein-rich phase and a watery phase, and is to a certain extent analogous to the salting out of alcohol. The first effect of concentrated salt is to withdraw water from the protein aggregates; a surface tension is in consequence developed at the interfaces, which causes the protein particles to aggregate, thus dividing the system into two distinct phases (precipitate and filtrate). The various factors which influence the precipitation are discussed at length; a dominating influence is the concentration of hydrogen ions.

W. D. H.

The Molecular Weight of Hæmin. HANS FISCHER and AMANDUS HAHN (*Ber.*, 1913, 46, 2308—2309).—Ebullioscopic measurements in pyridine solution indicate for hæmin a molecular weight of 651, and therefore a molecular formula $C_{54}H_{36}O_4N_4FeCl$; the trustworthiness of the method is confirmed by numbers indicating the molecular weight 655 for the complex iron salt of mesoporphyrin, $C_{54}H_{36}O_4N_4FeCl$.

The solution of free hæmatoporphyrin in pyridine appears to be colloidal, for the elevation in the b. p. of the solvent is so slight as to indicate a molecular weight over 3000 (compare Piloty and Dormann, A., 1912, i, 519).

D. F. T.

Hæmatin. III. Chemistry of the Formation of Hæmatoporphyrin. WILLIAM KÜSTER and PAUL DEHLE (*Zeitsch. physiol. Chem.*, 1913, 86, 51—76. Compare A., 1912, i, 670).—The age of hæmin preparations makes a considerable difference in their behaviour towards hydrogen bromide. Whereas freshly prepared hæmin yields almost exclusively hæmatoporphyrin and ferric iron, old hæmin preparations give both ferrous and ferric iron and much by-product. The changes in hæmin on keeping obviously take place at the centres which play a part in the formation of hæmatoporphyrin; these are considered to be the vinyl groups.

Hæmatoporphyrin is very readily esterified with methyl alcohol and hydrogen chloride. The product is a dimethyl derivative, insoluble in sodium carbonate, m. p. 142°, proving that the two carboxyl groups were present in hæmin, whereas the hydroxyl groups were formed

during the formation of hæmatoporphyrin. The ester is readily hydrolysed by sodium hydroxide.

A tetramethyl hæmatoporphyrin is obtained on prolonged heating with methyl alcohol and hydrogen chloride; the non-crystalline product has m. p. 81°.

A tetramethyl derivative is also obtained when the intermediate product formed by the action of hydrogen bromide in acetic acid on hæmin is warmed with anhydrous methyl alcohol. This substance, *methyl dimethoxydihydrohæmaterindicarboxylate*, forms large crystals, m. p. 128°.

On hydrolysis the tetramethyl derivative forms *hæmatoporphyrin dimethyl ether*, a bright scarlet, amorphous powder, m. p. 105°, soluble in alkali; the *hydrochloride* is crystalline, forming needles; the *zinc salt* is bright red, and blackens at 100°. When esterified, it yields the original tetramethyl compound again.

A further argument against the assumption that hæmin contains, as supposed by Piloty, lactam junctions is afforded by the discovery of a dimethoxydihydrohæmin amongst the products of the action of methyl alcohol on the above intermediate product.

Hæmatoporphyrin forms a silver salt containing two atoms of metal; its dimethyl ether forms one with three atoms of metal; both compounds fix three molecules of ammonia. Hæmatoporphyrin forms a stable dihydrochloride, whereas the hydrochloride of the dimethyl ether is very unstable, and that of the dimethyl ester could not be prepared. This behaviour indicates betaine formation between the nitrogen and the methyl group of the ester, and to a less extent the methyl group of the dimethyl ether. Prolonged action of concentrated hydrochloric acid displaces one of the methyl groups, forming a monomethyl ether, which, however, has a stable monohydrochloride.

The *dimethyl ester of anhydrohæmatoporphyrin* forms an intense scarlet, bulky powder, m. p. 140—141°. E. F. A.

Hæmatin. V. Methylation of Hæmin and the Addition of Bromine to Chlorodimethylhæmin and Bromodimethylhæmin. WILLIAM KÜSTER and ALFRED GREINER (*Zeitsch. physiol. Chem.*, 1913, 86, 185—205).—Dimethylhæmin is the dimethyl ester of the dibasic acid hæmin. Reasons are discussed for attributing a different degree of acidity to the two carboxyl groups, particularly the behaviour of hæmin to methyl sulphate. In strongly alkaline solution there is no action, in weak alkali a monomethyl derivative is formed, whereas in acid solution dimethylhæmin is formed without difficulty; it is identical with the product produced by means of methyl alcohol and hydrogen chloride. The monomethyl derivatives from hæmatin and dehydrochlorohæmin did not crystallise.

When bromine in chloroform solution acts on dimethylhæmin, bromine is absorbed without the liberation of hydrogen bromide; more or less of the chlorine of the hæmin is replaced by bromine, so that a complex mixture results. In acetic acid solution, however, a chlorodimethylhæmin dibromide is obtained. Very little of a tetra-bromo-product is formed. In a similar manner, bromodimethylhæmin dibromide is formed. It can be crystallised from acetic acid.

No methyl is eliminated by the action of aniline on dimethylhæmin. The dimethyl dehydrochlorohæmin so obtained is partly soluble in ether; the two portions differ in the amount of chlorine they contain. When converted into the corresponding bromodimethylhæmins, compounds which differ in their crystalline habit are obtained. Aniline reconverts both of these into dehydrobromo-products which are soluble and insoluble in ether respectively.

Bromine may be eliminated from hæmin dibromide by means of aqueous alkali, sodium methoxide, or by zinc and acetic acid. On oxidation one molecule of the dibromide yields two molecules of hæmatic acid. The conclusion is drawn that the addition of bromine takes place at the vinyl residues.

The complex $C_{52}H_{24}N_4$ is termed *haematerin*, and its dicarboxylic acid, $C_{34}H_{34}O_4N_4$, *haematerindicarboxylic acid*. Hæmin, bromohæmin, and hæmatin are thus complex chloro-, bromo- and hydroxy-ferric salts, of this acid. E. F. A.

Tetrachloromesoporphyrin. HANS FISCHER and HEINRICH RÖSE (*Ber.*, 1913, 46, 2460—2466).—On the cautious addition of fuming hydrochloric acid and hydrogen peroxide to mesoporphyrin dissolved in glacial acetic acid, the hydrochloride of a dye crystallising in green needles is obtained. This is *tetrachloromesoporphyrin*, chlorine being substituted for hydrogen in the four methine groups uniting the pyrrole nuclei in pairs. On reduction of the tetrachloro-compound with sodium amalgam, porphyrinogen is obtained, whereas mesoporphyrin results on heating with sodium methoxide at 220—230°. The green compound is also formed when chlorine is passed into a solution of mesoporphyrin in acetic acid. Reduction with acetic acid and hydrogen iodide converts it into mesoporphyrin again and not into porphyrinogen. One of the chlorine atoms is much less firmly held than the others. E. F. A.

Chondroitin-sulphuric Acid. PHOEBUS A. LEVENE and FREDERICK B. LA FORGE (*J. Biol. Chem.*, 1913, 15, 69—79).—Chondrosine, the nucleus of chondroitin-sulphuric acid, when hydrolysed by means of sodium amalgam yields glycuronic acid, identified by the phenyl- and *p*-bromophenyl-hydrazine derivatives.

The glycuronic acid is not bound to the amino-group of the second component, since the nitrous acid process demonstrates the presence of an unsubstituted amino-group in chondrosine. Neither does the carbonyl group of glycuronic acid take part in the linking. On oxidation of chondrosine with nitric acid a product is obtained which on distillation with hydrochloric acid gives rise to a minimal quantity of furfuraldehyde, whilst chondrosine yields the quantity required by a complex composed of one molecule of glycuronic acid and one of a carbohydrate of about the same molecular weight. The oxidation product does not contain free saccharic acid until it has been hydrolysed with alkali. Hence chondrosine contains saccharic acid

in a conjugated form. In chondroitin-sulphuric acid both the carboxyl and the amino-groups are combined with other radicles.

E. F. A.

Identity of Rennet, Casease, and Trypsin from the Same Latex. Existence of Two Types of Vegetable Proteolytic Ferments. C. GERBER (*Compt. rend.*, 1913, 157, 241—243. Compare A., 1907, i, 1100; 1908, i, 745; 1909, i, 74, 278; ii, 512, 824; 1910, ii, 64; 1911, ii, 647; 1912, ii, 801; this vol., i, 806).—Rennet, casease, and trypsin obtained from the same latex exhibit the same resistance to heat, and their diastatic actions are influenced in the same manner by certain electrolytes and by certain substances, such as lactalbumin and lactoglobulin, which accompany the substances on which they act. A study of these enzymes obtained from *Ficus carica* and *Broussonetia papyrifera* shows further that their diastatic actions obey the same laws of mass, time, and temperature, and their variations in intensity, seasonal for the same plant or individual for the same period, are strictly parallel. From these results the author maintains that rennet, casease, and trypsin from the same latex are but three different or successive aspects of the same diastase, coagulating the milk and carrying the hydrolysis of the casein and the fibrin to the formation of amino-acids. The characteristics distinguishing the three proteolytic actions of the latex are due to differences in the action of calcifying and decalcifying salts, acids, and bases on the coagulation and diastatic digestion of milk. The proteolytic ferments of the latex belong to two groups, the one having for type the proteolytic diastase of *Ficus carica* and the other that of *Broussonetia papyrifera*, the former being inactive towards milk, whilst the latter are active.

W. G.

Action of Hydrogen Chloride on a Diastase Preparation which had been Altered by Heating. IX. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, 86, 322—339).—A diastase preparation of which the activity had been destroyed by heating was rendered slightly active again by treatment with dry hydrogen chloride and subsequently removing this in a vacuum. It is considered that the original active groups in the enzyme have not been restored by the acid, but that this has attacked other atomic groupings, which become active as enzymes when the hydrogen chloride is removed.

E. F. A.

Identity of the Hydrolytic and the Synthetic Activities of Emulsin. ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], 8, 15—19).—Emulsin hydrolyses the β -glucosides of the alcohols and causes the combination of dextrose with the alcohol to a β -glucoside. Both these reactions are incomplete, and there is a tendency to attain an equilibrium. The position of this equilibrium is independent of the quantity of emulsin added and of the temperature, but it varies with the strength of the alcohol and with the amount of

dextrose present. It is shown experimentally that in a solution containing 30·2% by weight of methyl alcohol, and equivalent quantities of dextrose or β -glucoside together with emulsin, the rates of hydrolysis and synthesis are the same, and the same point of equilibrium is reached from both directions. The probability of emulsin acting synthetically in plants is emphasised. E. F. A.

Reversibility of Enzyme Action: α -Glucosidase and α -Methylglucoside. ÉMILE BOURQUELOT and ÉMILE VERDON (*J. Pharm. Chim.*, 1913, [vii], 8, 19—21).—Bottom yeast extract was allowed to act in solutions containing 20 grams per 100 c.c. of methyl alcohol and equivalent quantities of dextrose or α -methylglucoside. In about twenty-nine days both solutions had the same rotatory power, indicating that the same equilibrium is attained starting from either end. E. F. A.

The Rennin Coagulation of Milk from a Colloid Chemical Standpoint. JEROME ALEXANDER (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 12—14).—Silver nitrate gives a clear silver chloride sol in presence of fresh lactalbumin, but, after digestion with pepsin, lactalbumin does not exert the influence of a protective colloid. The action of acids or rennin on milk is thus to destroy the colloidal protection of the lactalbumin for the unstable, irreversible suspension, casein (compare A., 1910, i, 530). J. C. W.

New Function of the Catalyst termed "Peroxydase" and the Biochemical Transformation of Orcinol into Orcein. JULES WOLFF (*Eighth Inter. Cong. App. Chem.*, 1912, 26, 417—419. Compare A., 1912, i, 928).—Experiments are described which show that dilute solutions of orcinol are slowly oxidised by ammonia with production of orcein. This action is greatly accelerated by peroxydase, the effect of which is to promote the formation of the colouring matter rather than to increase the amount of oxygen absorbed. E. G.

The Catalase of the Liver. LEONOR MICHAELIS and H. PRECHSTEIN (*Biochem. Zeitsch.*, 1913, 53, 320—355).—The ferment solution employed was a highlydiluted extract of calves' liver, and hydrogen peroxide was used as the substrate. The course of the action was followed by determining the rate of destruction of the peroxide by titration with permanganate solution. It was found that for the catalase reaction, the ordinary equation $\Phi.t=f(x)$, where Φ is the quantity of the ferment, t = time of action, and $f(x)$ a characteristic function of the ferment, does not hold, but must be replaced by the equation $\Phi^n.t=f(x)$, in which n is of the approximate value of 1·35, but varies slightly during the course of the reaction. The deviation from the ordinary law is due to the fact that the ferment is acted on by the hydrogen peroxide, as its action is weakened by previous treatment with this reagent. Oxygen itself does not act, and the same results are obtained when the reaction is carried out in a current of hydrogen

or in a corked flask. As determined by the wandering of the ferment in an electrical field, where the $[H]^+$ concentration was varied by different acetate mixtures, the isoelectric point of the ferment was found to be $4.31 \cdot 10^{-6}$. The rate of ferment action was determined in low salt concentrations (acetate mixtures) with varying hydrogen-ion concentrations. By the graphical methods already employed by Michaelis and his pupils, the amounts of ferment active in solutions of different hydrogen-ion concentrations were determined. The optimal condition of action is attained just after the hydrogen-ion concentration becomes less than the isoelectric point of the ferment. The conclusions drawn are, that catalase is an ampholyte with the acid dissociation constant 2.88×10^{-5} , and that the catalytic action on hydrogen peroxide is due to the anions and electrically neutral particles. Neutral salts inhibit the action (hence all the experiments on the effect of the $[H]^+$ concentration were carried out with very dilute acetate mixtures). The inhibitory action is more marked in the neighbourhood of the isoelectric point than in more acid solutions. The conclusion is drawn that the anions of the salt exert the chief action, and affect chiefly the electrically neutral particles of the ferment. The order of the inhibitory action is $SO_4 > Cl > acetate > NO_3$. S. B. S.

Constitution of the Mercuriated Products of Acetylene.
WILHELM MANCHOT and JULIUS HAAS (*Annalen*, 1913, 399, 123—154).—Phenylacetylene and an excess of aqueous mercuric chloride at $47-50^\circ$ yield a substance, $C_{10}H_{11}O_2Cl_3Hg_2$ or $C_{10}H_{13}O_3Cl_3Hg_2$, in which the mercury is very firmly held. It does not react with aqueous sodium hydroxide or ammonia, but yields mercuric sulphide by treatment with ammonium sulphide. By treatment with dilute hydrochloric acid, it yields phenylacetylene and acetophenone. This decomposition indicates that the substance is an additive compound of an acetylene, not a mercuriated ketone, and consequently the constitution may be $Hg(C\equiv CPh)_2 \cdot 2HgCl_2 \cdot HgO \cdot HgCl \cdot OH$, which is supported by the fact that the same substance is produced by the action of an excess of aqueous mercuric chloride on mercury phenylacetylide in the presence of a little hydrochloric acid at 50° .

A similar substance, $C_{10}H_{10}OBr_4Hg_2$, is produced by the interaction of phenylacetylene and aqueous mercuric bromide at 50° . It also does not react with sodium hydroxide or ammonia, yields mercuric sulphide by treatment with ammonium sulphide, and is decomposed by hydrochloric acid to form acetophenone and phenylacetylene. Probably, therefore, its constitution is $Hg(C\equiv CPh)_2 \cdot 2HgBr_2 \cdot HgO$. Both of these substances, suspended in chloroform in a freezing mixture, absorb a large amount of bromine; ultimately, however, hydrogen bromide is evolved.

Piperonylacetylene reacts with mercuric chloride and bromide to form substances which are analogous to the preceding, but which yield only acetopiperone by treatment with hydrochloric acid. This is due to the fact that the piperonylacetylene which is initially formed unites with water with extraordinary ease in the presence of hydrochloric acid.

Since the preceding substances are additive compounds of acetylenes,

it is probable that the substance obtained by the action of acetylene itself on aqueous mercuric chloride is an additive compound, not a mercuriated aldehyde, $C(HgCl)_3 \cdot CHO$, as suggested by Biltz and Mumm. The latter view is almost certainly incorrect, because the substance exhibits the reactions of mercurous and of mercuric salts. The substance, which is also obtained from mercury acetylide and aqueous mercuric chloride, yields only acetaldehyde by treatment with dilute hydrochloric acid, but is decomposed by ammonium sulphide to form acetylene and acetaldehyde. Probably, therefore, its constitution is $C_2Hg, HgCl_2, HgCl, H_2O$. A substance, exhibiting properties similar to those of the preceding substance is obtained from acetylene or mercury acetylide and an excess of aqueous mercuric bromide.

It is evident from the behaviour of the preceding mercury compounds that mercury can be retained very firmly in an organic compound without necessarily being attached to carbon in the place of hydrogen atoms.

C. S.

Physiological Chemistry

A Calorimeter for Small Animals. FRANZ TANGI. (*Biochem. Zeitsch.*, 1913, 53, 21—35).—The calorimeter is constructed on the compensation principle. Two exactly similar cylinders of copper, each insulated in a Dewar flask, are connected with one another by constantan wires, so as to form thermoelectric couples, and a Broca galvanometer is placed in circuit between the two, so as to indicate any differences of temperature between them. The whole apparatus is immersed in a large thermostat. The animal is placed in one cylinder in a cage, and the other cylinder contains a similar cage without an animal. The heat produced by the animal in one cylinder is approximately compensated for by the passage of a known electric current through the other, which produces an experimentally measurable quantity of heat. The small differences of heat in the two cylinders can be measured by the deflexions produced when the galvanometer is thrown into the circuit. The galvanometer deflexions can be calibrated by passing two measured but slightly different currents through the two cylinders. The total heat produced by the animal is therefore calculated both from the compensation current and the galvanometer readings; the calorimeter can also serve as a respiration calorimeter, by the analysis and measurement of the air led in (which is first carefully warmed to the temperature of the thermostat by a long passage through pipes immersed in the water it contains), and the analysis of the expired air, in the usual manner adapted for such calorimeters. Illustrations in the text indicate the exact method of construction of the apparatus (compare A. V. and Miss Hill, this vol., i, 666).

S. B. S.

The Response of the Respiratory Centre to Carbon Dioxide, Oxygen, and Hydrogen Ion Concentration. J. M. H. CAMPBELL, CLAUDE E. DOUGLAS, JOHN S. HALDANE, and F. G. HOBSON (*J. Physiol.*, 1913, 46, 301—318).—A rise of 0.2% or 1.6 mm. in the pressure of carbon dioxide in the alveolar air doubles the pulmonary ventilation. A corresponding diminution causes apnoea. The alveolar oxygen pressure can be varied within wide limits without affecting the excitability of the respiratory centre to carbon dioxide. Summation of inhibitory vagus stimuli plays no part in causing apnoea in man. What the respiratory centre really responds to is the balance of hydrogen ion concentration in the blood. This balance is exquisitely regulated, probably for the most part by the kidneys.

W. D. H.

Respiratory Mechanism in the Duck. J. B. ORR and ALEXANDER WATSON (*J. Physiol.*, 1913, 46, 337—348).—In the duck, carbon dioxide in the inspired air acts inhibitingly on respiration. Lack of oxygen is stimulating to the respiratory rhythm. The vagus nerves probably play an essential part in the maintenance of respiratory movements.

W. D. H.

The Influence of the Cerebrum on the Metabolism of Energy and of Matter. KARL HANNEMANN (*Biochem. Zeitsch.*, 1913, 53, 80—99).—The experiments were carried out on frogs, the respiratory exchanges of which were measured in chambers made according to a method described in the text, from ordinary laboratory desiccators. These exchanges were measured in the cases of intact animals, and animals from which different parts of the brain had been extirpated. It was found that the extirpation of either the whole brain, or only the large hemispheres, or the optic lobe led to a considerable increase in the gaseous exchange, lasting for several days. Both the oxygen consumption and the carbon dioxide output were increased, especially the latter, which was not so much increased, however, when only the hemispheres were removed. The increase in the gaseous exchanges is accompanied by an increased heat production, which was measured in a Tangl calorimeter.

S. B. S.

The Influence of Narcosis on the Gaseous Metabolism of the Brain. FRANZ G. ALEXANDER and STEPHAN CSERNA (*Biochem. Zeitsch.*, 1913, 53, 100—115).—Dogs were used for the purpose of the experiments. They were tracheotomised under ether narcosis, hiradin was injected into the jugular vein and the femoral artery, and the sinus longitudinales was laid bare for the purpose of collecting blood samples. By means of blood-gas analyses, the gaseous metabolism could be determined when the animal had recovered from narcosis, and when it was under the influence of various anaesthetics. The rate of blood-flow was measured by Barcroft's method. It was found that the specific gaseous exchanges of the blood were considerable, the oxygen consumption of this organ being about 0.36 c.c. per gram per minute. During

narcosis the gaseous metabolism sinks considerably—from 60 to 90% according to depth of the narcosis. With ether, the carbon dioxide output diminishes less than the oxygen consumption; the reverse is the case in morphine narcosis. The action of various narcotics is different, and this fact must be taken into account in all theories dealing with the phenomenon. In narcosis with magnesium sulphate, the higher centres of the nervous system are the last to be paralysed. The actual narcosis is preceded by a stage of excitation, during which the gaseous metabolism of the brain is increased.

S. B. S.

Blood lipoids and Phagocytosis. B. STUBER (*Biochem. Zeitsch.*, 1913, 53, 493—500).—The addition of cholesteryl esters of oleic and palmitic acids inhibits phagocytosis *in vitro*, and with the latter substance also *in vivo*, when the blood is withdrawn (from cats) half an hour after the injection. Owing to the rapidity with which clot formation takes place, experiments could not be extended beyond this period, and for the same reason no *in vivo* experiments were possible with the oleic acid derivative, which very readily renders the blood so clottable that it clots directly on opening the veins. The inhibition is not removed by mixing the cholesterol derivatives with lecithin, as is the case with free cholesterol. Cholesteryl benzoate and acetate are without action on phagocytosis, in which substances the free hydroxyl group no longer exists, and to this group is ascribed the inhibitory action of cholesterol and its derivatives on phagocytosis. Wright's theory of opsonins is discussed, and it is suggested that the opsonic index is not due to specific opsonins, but rather to the different states of the lipoids in the blood.

S. B. S.

The Effect of Fatty Acids and Soaps on Phagocytosis HARTOG J. HAMBURGER and J. DE HAAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1290—1297).—Propionic acid itself diminishes phagocytic action (as determined by Hamburger's charcoal method), whereas sodium propionate increases it, within wide limits of concentration of the salt. The former action is to be ascribed to the hydrogen ions, whereas the latter action is due to the action of the salt on the surface tension of the water. This constant is diminished, and this facilitates the pseudopodial action of the phagocytes. This action of sodium propionate and soaps is to be distinguished from the action of fat-dissolving substances, which exert their action owing to the fact that they dissolve in lipoids.

S. B. S.

The Blood of Ascidians. III. MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1913, 86, 340—344).—The author's previous work has shown that organic vanadium compounds occur in the blood-corpuscles of Phallusia, and that these cells have an acid reaction due to sulphuric acid. It is now shown that vanadium also occurs in the blood of other ascidians (*A. mentula*, *A. fumigata*, *Ciona intestinalis*, and *Diazonia violacea*); in *Cynthia papillosa* its presence is uncertain.

Much of the present paper deals with the kinds of blood-corpuscle found, and their reactions with staining fluids. The nature of the pigment in the red cells of *Ascidia mentula* is uncertain; it is not a lipid, and is insoluble in all common reagents.

W. D. H.

The Application of the Second Law of Thermodynamics to Processes in the Animal Organism. JULIUS BARON and MICHAEL PÓLÁNYI (*Biochem. Zeitsch.*, 1913, 53, 1—20).—A knowledge of the changes of free energy in the animal organism can be arrived at by the application of Nernst's heat theorem. These changes of free energy were calculated for the individual products taking part in metabolism. It was found that the changes correspond very nearly with the heat production. The results indicate that the processes in the organism take place in accordance with the second law of thermodynamics only when the organism does not work with absorption of heat. The thermodynamical efficiency of mechanical work and of fat-synthesis from sugar was calculated, and the trustworthiness of the theory from the point of view of the second law was confirmed.

S. B. S.

The Influence of the Character of the Nutrition on the Metabolism During a Succeeding Period of Starvation. ARTHUR SCHLOSSMANN and HANS MÜRSCHHAUSER (*Biochem. Zeitsch.*, 1913, 53, 265—299).—Dogs were starved for some days, and then fed with different diets, in one case containing large amounts of fats, in another large amounts of carbohydrates, and in a third case, chiefly proteins. When the animals had attained their original weights again on these diets, a short period of starvation was interposed, during which the metabolism was investigated by the ordinary methods. As a result of these and earlier experiments, the conclusion was drawn that the metabolism during a period of starvation in both man and dogs depends to a large extent on the character of the nutrition ingested in the foregoing period, and this influence can be demonstrated even when the effects of the last meal taken have vanished. The organism has got accustomed to the utilisation of either fats, carbohydrates, and proteins, and the habit thus acquired still lasts even when the animal is deprived of food. This influence is demonstrated chiefly by the respiratory quotients, which remain similar during starvation to those obtained during the period of feeding. The influence of the fat diet lasts longer than that of the carbohydrate diet, as the reserve glycogen is soon used up. Thus, in the case of the dog fed on fats, on the fifth as well as on the second day of starvation about 90% of the calories are derived from the fat, and 3% from carbohydrates. In the case of the carbohydrate-fed dog, on the second day of starvation 21% of the calories are derived from carbohydrates, and 65% from fats; and on the fifth day, only 8% from carbohydrates and 79% from fats. The organism can therefore be "trained" to adapt itself to various diets.

S. B. S.

VOL. CIV. i.

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The Action of Carbohydrates on the Energy Metabolism. PAUL HÄRI (*Biochem. Zeitsch.*, 1913, 53, 116—139).—The experiments were carried out with the employment of the Tangel respiration calorimeter, and both the heat production and the nitrogen and carbon metabolism were investigated at the same time. When dextrose was subcutaneously administered to mice in 10% solution, in quantities corresponding with 10 grams per kilo. of body-weight, it caused a rise in the heat production of 8—13.2%. In quantities of 28—32 grams per kilo. of body-weight, when administered to starving rats, it caused a rise of 28—29.9%. This rise can be partly explained as a result of sugar intoxication. The heat thus produced is chiefly lost by radiation when the sugar is administered in concentrated solutions, but chiefly by water evaporation when given in dilute solution. S. B. S.

The Biochemical Synthesis of the Fatty Acids. (Miss) IDA SMEDLEY and (Miss) EVA LUBRZYNSKA (*Biochem. J.*, 1913, 7, 364—374).—The hypothesis that pyruvic acid formed in the body from carbohydrates is the starting point for the synthesis of the fatty acids, is supported by a number of pieces of evidence, and equations are given to represent the series of reactions which occur W. D. H.

Fatty Acid Esters of Dextrose. W. R. BLOOR (*English Inter. Cong. App. Chem.*, 1912, 19, 29—36).—Attention is called to the fact that fats are not completely metabolised in the absence of carbohydrates, as is witnessed by the fact that such products as β -hydroxybutyric acid, acetoacetic acid, etc., are excreted during starvation. The suggestion is made that sugars may act catalytically in the destruction of the fats in the animal body. It was therefore of interest to prepare dextrose esters of fatty acids and to investigate their action when administered to animals. These esters were prepared by the interaction of the acid chloride on dextrose in pyridine solution, and a preliminary account of several such esters is given. They readily form colloidal solutions with water. For physiological experiment a mixture of the esters prepared from the fatty acids of cocoa-nut oil was employed. When administered to cats by the mouth, these esters are readily absorbed (up to more than 80%). They do not appear to be adapted to administration either intraperitoneally or intravenously. In the former case, they act as an irritant foreign substance, and in the latter case they can act injuriously, even producing death of the animal. S. B. S.

Is Inulin a Glycogen Former? ALFRED OPPENHEIM (*Chem. Zentr.*, 1913, ii, 371; from *Zentr. Physiol.*, 1913, 27, 264—267).—Rabbits freed from glycogen by injections of strychnine were fed with inulin. Some glycogen was formed in the liver, and a good deal in the muscles. Since feeding with laevulose leads to the formation of glycogen in the liver, it is assumed that most of the inulin administered passes the liver and is converted into glycogen in the muscles. E. F. A.

Action of the Digestive Juices on Alicyclic Compounds.

JUHO HÄMALÄINEN (*Chem. Zentr.*, 1913, i, 2052; from *Skand. Arch. Physiol.*, 1913, 29, 60—67).—When alicyclic compounds are shaken for ten hours at 37° with gastric juice, they become partly hydrated—the hydrocarbons the most easily, and the ketones the least so. Menthene, limonene, terpinolene, pinene, nopinene, and dihydrocarveol give rise to menthanol, terpin, terpineol, etc. Only terpinene and fenchene proved resistant.

E. F. A.

Influence of the Melting Point of Non-emulsified Fats on their Rate of Disappearance from the Stomach.

A. VON FEJÉR (*Biochem. Zeitsch.*, 1913, 53, 168—178).—Various fats were mixed with a standard diet and administered to dogs. After a given interval these test-meals were quantitatively removed from the stomachs by a form of stomach-tube, which is described and illustrated in the text, and the fat content of the vomit was then analysed. It was found that the higher the melting point and viscosity of the fat, the more slowly it disappeared from the stomach. The fats, after emulsification with food, disappear more rapidly than when administered in a non-emulsified form. When not administered with foods, these disappear even more slowly still, with the exception of the liquid olive oil. Fats also inhibit the disappearance of the other food constituents from the stomach, and the more viscous fats exert the greater inhibitory action in this respect. A fat added to foods readily separates from other food constituents in the stomach, and is afterwards digested independently of them in the intestine.

S. B. S.

The Influence on Nitrogenous Metabolism of Feeding on Sodium Nitrate.

ERICH GRAFE and H. WINTZ (*Zeitsch. physiol. Chem.*, 1913, 86, 283—314).—Experiments on dogs and pigs are recorded with sodium nitrate similar to those previously published in relation to ammonium salts. In one of the four experiments there was no retention of nitrogen; in the other three, from 10—15% of the nitrogen was retained. Large doses exert a toxic action and increase the output of nitrogen. Hypotheses are advanced to explain the retention of nitrogen.

W. D. H.

Utilisation of Individual Proteins by Man as Influenced by Repeated Fasting.

PAUL E. HOWE and PHILIP B. HAWK (*Eighth Inter. Cong. App. Chem.*, 1912, 19, 145—147).—The method of experiment was to administer to the same individual after a two days' fast, a standard diet containing 12.12 grams of nitrogen and 2500 cal. of energy. This diet was continued for two days, and was then increased for another two days, so that 18.18 grams of nitrogen and 3750 cal. were taken. Two days' fast then succeeded, and was followed by another five days of feeding with the quantities given above, but with nitrogen from another protein. By alternation of two fast days and five feeding days, in which various proteins were employed, the dietetic values of the latter

could be ascertained. The most efficiently utilised proteins were found to be meat and gliadin, of which 97.5% was absorbed, followed by plasmon, milk, and "standard" diet. The substances most efficient in maintaining a nitrogenous equilibrium (in both cases under the conditions of experiment, positive) were, however, meat and milk. It is noteworthy that in both cases the proteins were of animal origin.

S. B. S.

Nuclein Metabolism. MAX DOHRN (*Zeitsch. physiol. Chem.*, 1913, 86, 130—136).—The results of an experiment in which 10 grams of nucleic acid were consumed in addition to a diet consisting of bread, 300 grams; butter, 80 grams; apples, 250 grams; eggs, 200 grams, and milk, 2 litres, showed that the nitrogen in the form of carbamide is not increased during the nucleic acid period. The nitrogen in uric acid increased 50%, or 9.7% of the nitrogen in purine bases. The rest of the nitrogen as purine bases was not recovered. The phosphoric acid increased considerably, the amount found in the urine and faeces exceeding the amount supplied by 0.76 gram. The results indicate that almost all the nucleic acid underwent cleavage before resorption, and that the slight increase in uric acid is due to resorbed bases.

N. H. J. M.

The Action of the Iron in Blood-powder on the Iron Metabolism when this Product is Administered to Animals. JULIUS GRÖN (*Biochem. Zeitsch.*, 1913, 53, 256—258).—By the addition of blood-powder to a standard diet administered to pigs, no alteration was caused in the iron balance in the animal, the additional iron from the blood ingested being excreted in the faeces.

S. B. S.

The Localisation and Detection of Peroxydases in the Digestive Tract. ARTHUR SCHEUNERT, WALTER GRIMMER, and PETER ANDRYEWSKY (*Biochem. Zeitsch.*, 1913, 53, 300—319).—A trustworthy oxydase reagent is guaiacol tincture, to 100 c.c. of which have been added 0.1—0.2 c.c. of 3% hydrogen peroxide solution. This reagent is capable of detecting an oxydase in milk, saliva, etc., which contain a peroxydase, but not with blood, unless a superoxide solution, such as turpentine oil, ethyl hydroperoxide, etc., is also added. Rothenfusser's reagent (*p*-phenylenediamine + guaiacol) and the potassium iodide-starch reagents are not trustworthy for the detection of oxydases. The extracts of tonsils contain no oxydase, the sublingual glands contain large quantities of the ferment, whereas the submaxillary and parotid glands vary largely as to oxydase content in different animals; the same is true with reference to the mucous membrane of the stomach and the small intestine. Liver extracts are free from substances giving the blue reaction with guaiacum tincture. Furthermore, the ferment giving this reaction is not identical with the ferment causing the oxidation of formic acid, as several tissues give one reaction, but not the other. The guaiacol peroxydase of the submaxillary gland of the ox possesses a considerable but not complete resistance to digestion with trypsin.

S. B. S.

Fluorine in the Animal Organism. III. Brain, Glands, Muscles, Blood, Milk, Excretions. ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1913, 157, 94—100. Compare this vol., i, 677, 789).—Like phosphorus, fluorine exists in all animal organs and tissues, but in very varying proportions, the dental enamel having the highest content, 180—118 mg. per 100 grams of dry matter, and the muscle the lowest with 0.6—0.15 mg. per 100 grams. There is a fairly constant relation between the phosphorus and fluorine contents of the various organs, except in the case of the incompletely formed organs of young animals, the excretions, the dental enamel, and the blood. The fluorine increases with the phosphorus without being directly proportional to it. In the same organ the quantity of fluorine varies greatly with age. It increases generally up to the adult age, and then diminishes as the organ begins to degenerate. Muscular tissue is remarkably poor in fluorine. The fluorine content of human milk is very low, but, as in the case of phosphorus, it is about four times as great in cow's milk. About 1 mg. of fluorine per day is excreted by man, and since the amount of fluorine supplied by the food greatly exceeds this, the difference must be due to epithelial desquamation, loss of hair, growth of nails, etc. W. G.

The Lipocytic Constant. Content of the Tissues in Phosphorus-containing Lipoids. ANDRÉ MAYER and GEORGES SCHAEFFER (*Compt. rend.*, 1913, 157, 156—159. Compare this vol., i, 424).—In different individuals of the same species the content of phosphorus in the lipid form in a given organ is practically constant, but it varies from tissue to tissue in the same animal. For different animal species the values found for a given organ are very close. This phosphorus content of the different organs does not seem to vary during inanition, but rather appears to be the measure of a fundamental and permanent constituent of the cells. In certain cellular types the ratio, fatty acids/phosphorus in lipid form, is remarkably constant, but in certain organs, for example, the muscles, the ratio has a value pointing to the presence of reserves of neutral fats in these organs. The content of a fresh tissue in phosphorus, in lipid form, is characteristic of the tissue. In all the species examined the order of the different organs with respect to their phosphorus content relative to their fresh weight is the same, and this indicates that this content is proportional to the physiological activity. W. G.

The Application of Calorimetry to the Measurement of the Work of the Kidneys. FRANZ TANGL (*Biochem. Zeitsch.*, 1913, 53, 36—40).—The energy metabolism of the kidneys was estimated by determining the heat production of rats placed in a calorimeter both before and after the extirpation of the kidneys. This was found to amount to 8.2% of the whole energy production of the body, and about 0.75 cal. per gram of kidney. This is the same as that found in the dog. Direct calorimetric measurements yield the same results as those obtained by Barcroft's method in the

analysis of the blood gases, and the author's own methods in the measurement of respiratory exchanges in curarised animals.

S. B. S.

The Magnitude of the Work of Diseased Kidneys. STEPHAN CSERNA and G. KELEMEN (*Biochem. Zeitsch.*, 1913, 53, 41—68).—The respiratory method of Tangl was employed in these researches, the respiratory exchanges of the animal being measured both before and after extirpation of these organs in animals which had been treated with renal poisons. These results were compared with those obtained in the normal (unpoisoned) animals. Dogs were used in the experiments, and the following poisons were employed: uranyl acetate, potassium cantharidate, potassium dichromate. Experiments were also carried out on animals, in which the blood-supply to the kidneys had been ligatured. It was found that the work of the diseased kidneys was greater than that of healthy ones, the oxygen consumption and carbon dioxide production both being larger. Only when the poison had been sufficiently powerful to produce anuria were these factors below normal. When the kidney work is increased, both the absolute and relative carbon dioxide production is greater than normal in diseased kidneys. By injury to the parenchyma of the kidney tissue produced by the stoppage of the circulation, the gaseous metabolism in the other organs is also increased.

S. B. S.

The Magnitude of the Work of the Spleen. FRITZ VERZAR (*Biochem. Zeitsch.*, 1913, 53, 69—79).—No alteration can be detected with certainty in the respiratory exchange after extirpation of the spleen of curarised dogs. By the direct measurement of the gaseous exchange in the blood passing through the spleen of cats by Barcroft's method, the oxygen consumption was found to be 0.05 c.c. of oxygen per gram per minute. This is about the same as that of the resting submaxillary gland or anuric kidneys, according to the researches of Barcroft. Dextrose, intravenously injected, and soluble starch are readily burnt up in the body, even after extirpation of the spleen.

S. B. S.

The Changes in the Chemical Constitution of the Animal Body After Extirpation of the Spleen, Testis, and Thyroid. KARL DRÜGE (*Pflüger's Archiv*, 1913, 152, 437—477).—The experiments were performed on dogs during the suckling period. Extirpation of the spleen delays growth, but whether this is the result of removing the organ or of the operation of laparotomy is uncertain. An increase of total ash (especially in calcium and to a smaller degree in phosphoric acid) was the only chemical change in the body noted. Extirpation of the thyroid does not affect growth, and causes a decrease in total ash. Extirpation of the testis does not affect growth, and a small decrease in the phosphoric acid of the ash occurs. Water, fat, fat- and ash-free substance, and proteins are not affected in all these classes of experiments.

W. D. H.

Muscle Chemistry. IV (Addendum). The Muscle Tissues of some Sea Animals when Dried by Heat. GIUSEPPE BUGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1913, 86, 137—140. Compare this vol., i, 219).—When dried at 100—102°, the muscle tissues of some sea animals lose substances having an alkaline reaction, produced by the decomposition of extractive substances. At a temperature of 110—112°, acid substances are lost.

In the case of *Scyllium catulus* it was found that the loss is chiefly to be attributed to ammonia, produced by the decomposition of carbamide. N. H. J. M.

Catalase in Frogs' Muscles. EINAR HAMMERSTEN (*Chem. Zentr.*, 1913, i, 2051; from *Skand. Arch. Physiol.*, 1913, 29, 46—59).—The action of a number of products of normal metabolism on the system catalase-hydrogen peroxide is investigated in a specially devised apparatus, frogs' muscles being used as the source of enzyme (compare Santesson, A., 1908, ii, 1061; 1910, ii, 331). The addition of creatinine causes a rapid increase in the rate of action at first; subsequently it falls owing to the using up of the peroxide. Creatinine decreases the rate of change similarly to Siegfried's "phosphor-meat acid." Choline hydrochloride and muscarine platinichloride have a direct harmful action on the enzyme. Acetaldehyde likewise lowers the activity, but reacts with hydrogen peroxide, fixing oxygen. Carbamide and alcohol are without effect. The muscle enzyme was more active in July and August than during December to June. When several substances act at once on the enzyme, the rate of change curves lie between those of the several constituents. E. F. A.

Influence of Various Substances on the Gaseous Interchange of Surviving Frog's Muscle. XI. Action of Aromatic and Other Cyclic Compounds. TORSTEN THUNBERG (*Chem. Zentr.*, 1913, i, 2054; from *Skand. Arch. Physiol.*, 1913, 29, 1—28. Compare A., 1911, ii, 56, 627).—The behaviour of a number of benzene derivatives on the gas exchange of surviving muscles is described. Monobasic carboxylic acids, such as benzoic acid and the toluic acids, lessen the exchange; hippuric acid behaves similarly, but is weaker. The introduction of a second carboxyl group overpowers the adverse influence of the first. Phthalic acid is hardly poisonous, isophthalic and terephthalic acids are slightly more so, and mellitic acid is very slightly poisonous. β -Phenylpropionic acid is as poisonous as phenylacetic acid. When the carboxyl group is in an unsaturated side-chain, the adverse effect on the exchange is much increased; this is exemplified by the behaviour of cinnamic, *all*ocinnamic, β -benzylidenepropionic, phenylpropionic, and phenylmalonic acids. The salicylic acid grouping is more poisonous than the benzoic acid grouping. The para-compound is the least poisonous of the three hydroxytoluic acids. Anisic acid as a methoxy-compound is less poisonous than *p*-hydroxybenzoic acid. The presence of several hydroxy-groups does not greatly alter the action of the aromatic acids. The phenol-alcoholic acids, for

example, mandelic and phenylparaconic acids, are almost without effect.

Phenols are less poisonous than benzoic acid. It is considered that the benzene ring as such has a poisonous action on certain constituents of the cell concerned in the normal respiratory process. Nitration, as in mono- and di-nitrobenzoic acids, has little effect on the physiological action; sulphonation lessens the poisonous character of the ring. On the other hand, the hydrated six-membered ring in inositol and camphoric acid is inactive. The introduction of nitrogen into the ring, as in picolinic, nicotinic, and quinolinic acids, also counteracts the poisonous effect. Quinoline, which contains both pyridine and benzene nuclei, is strongly poisonous. Five-ring compounds are moderately poisonous.

E. F. A.

Organic Bases in the Roe of Herrings. KIYOHISA YOSHIMURA (*Zeitsch. physiol. Chem.*, 1913, 86, 174—177).—The dry matter (92.093%) of the herring roe had the following composition: total N, 12.063; crude fat, 1.253; total P, 0.602; P as lecithin, 0.200; N as proteins, 0.601; N as ammonia and amines, 0.338; N as bases, 0.244%. One kilo. of the dried substance yielded 0.12 gram of trimethylamine, 0.02 gram of tetramethylethylenediamine, and 0.70 gram of choline.

N. H. J. M.

The Occurrence of Free Sulphuric Acid in the Mantle of *Ascidia mentula*. MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1913, 86, 345—346).—The cellulose mantle of *A. mentula* is acid, and this is due to sulphuric acid in the "bladder cells" of the mantle. Whether this is related to the acid cells of the blood is uncertain, for in *Phallusia mamillata*, although the blood-cells are acid, there is no acid in the mantle. There is less total sulphate in the expressed juice of *Phallusia* mantle than in the sea-water. The amount of chlorides in the two is equal.

W. D. H.

Presence of Carbamide in the Invertebrates and in their Excretion Products. ROBERT FOSSE (*Compt. rend.*, 1913, 157, 151—154. Compare A., 1912, ii, 1203; this vol., i, 327, 432).—The author has proved the presence of carbamide in numerous invertebrates and their excretion products, and also in the water inhabited by them for any length of time, as follows:

Coelenterata: Actinia, and its products of excretion.

Echinoderm: Starfish, and products of excretion.

Worms: *Sangsue officinale*, cellular juice, and products of excretion.

Crustaceæ: Crayfish, cellular juice of the entire animal, of the flesh deprived of the organs, and of the liver; also in the products of excretion; spiny lobster, cellular juice, and excretion products; shrimp, cellular juice.

Insects: Silkworm, cellular juice; ant, eggs; fly, eggs.

Molluscs: Snail, entire animal, products of secretion and excretion; mussel, liquid in the shells; oyster, liquid in the shells.

W. G.

The Mechanism of the Physiological Production of Light; Luciferase, Luciferin, and Luciferescence. RAPHAEL DUBOIS (*Eighth Inter. Cong. App. Chem.*, 1912, 19, 83—89).—Phosphorescence in organisms is due, according to the author, to the interaction of two substances, which he has isolated more especially from the molluscular lamellibranch, *Pholades dactylus*. One of the substances, to which the name *luciferin* is given, can be extracted from the secreting organs by water, after heating to 70°, at which temperature it is stable. The other substance, *luciferase*, is, however, destroyed at 60°. By the action of one on the other in the presence of air, a phosphorescence is produced. The luciferase is of ferment-like character (oxydase), and it can be replaced by an oxidising agent, such as potassium permanganate, and by the blood of various cold-blooded animals, such as molluscs and marine crustaceans. Solutions of both substances give protein reactions, and the luciferin contains phosphorus and can be precipitated by picric acid. The term luciferescence is adopted for the fluorescent substances in other animals, such as the fire-fly (compare McDermott, A., 1911, i, 396).
S. B. S.

Indian Edible Swallows' Nests. HEINRICH ZELLER (*Zeitsch. physiol. Chem.*, 1913, 86, 85—106).—The substance, dried in a vacuum, contained 9.43% of total nitrogen, 1.35% of histidine, 1.20% of arginine, and 1.18% of lysine. When hydrolysed with 4% sulphuric acid, two reducing substances, not identified, were obtained.
N. H. J. M.

The Ferments of the Milk Glands and of Milk. WALTHER GRIMMER (*Biochem. Zeitsch.*, 1913, 53, 429—473).—Both in resting and active milk glands proteoclastic ferments are present, which can digest the proteins of the glands themselves, but not other proteins, such as fibrin, gelatin, egg-white. Glycine, leucine, and other products of hydrolysis were formed. Tryptophan was found as hydrolysis product of the active, but not of the resting gland. The expressed juices, saline extracts, and autolysates of both resting and acting glands contain a peptoclastic ferment, which can set free tyrosine from milk peptone. Reasons are given for supposing that the peptoclastic and proteoclastic ferment are not identical. The active and resting glands contain a monobutyrylase, the activity of which is considerably weakened by dialysis. The milk glands of the ox and pig possess an amylolytic ferment both when active and resting. In the case of the cow, the amylolytic ferment is more active in the resting than in the active gland, whereas the resting glands of sheep possess no marked amylolytic capacity. All glands (expressed juices and saline extract) possess a ferment capable of hydrolysing salol, and it is shown that this action is not due to the alkalinity of the medium. A guaiacum peroxidase was only found in the lactating glands of ruminants. This is apparently not identical with the *p*-phenylenediamine oxydase, as no parallelism was found between the two ferments in the various glands, etc., investigated.
S. B. S.

The Quantity of Alcohol Excreted by the Animal Organism Under Various Conditions. IV. The Influence of Dose and External Temperature on the Excretion of Alcohol by the Urine and Expired Air; the Absorption of Alcohol from the Urinary Bladder. WILHELM VÖLTZ and AUGUST BAUDREXEL (*Pflüger's Archiv*, 1913, 152, 567—578. Compare A., 1912, ii, 466).—In doses of 3 c.c. of alcohol per kilo. of body weight in dogs, from 92 to 98% is oxidised in the body; at a low external temperature the figure is higher (96% at 16°, and 92% at 26°). A certain amount of alcohol is absorbed from the bladder when the concentration in the urine is not greater than the quantity found there after its ingestion.

W. D. H.

Respiration and Metabolism in Cardio-renal Disease. THOMAS LEWIS, JOHN H. RYFFEL, CHARLES G. L. WOLF, T. COTTON, G. L. EVANS, and JOSEPH BARCROFT (*Proc. physiol. Soc.*, 1913, liii—lv; *J. Physiol.*, 46).—The fundamental factor in such cases is an increase in the proportion of acids (exclusive of carbon dioxide) in the blood. There is a fall in the alveolar carbon dioxide, and meionexy.

W. D. H.

The Combustion of Sugar in Pancreas Diabetes. FRITZ VERZAR and A. VON FEJÉR (*Biochem. Zeitsch.*, 1913, 53, 140—167).—Experiments were carried out on curarised tracheotomised dogs, with the object of ascertaining whether, after extirpation of the pancreas, the intravenous injection of sugar still caused a rise in the respiratory quotient, which serves as an indication that the sugar is being burnt in the body. Such a rise occurred up to the fourth day after the operation, after which no sugar was burnt up. In certain cases, when the animal is thus rendered diabetic, sugar injection causes a rise in oxygen consumption, but in others it does not. Neither by blood transfusion from another animal, nor by infusion of ordinary blood or of blood from the pancreas, could a rise in the respiratory quotient after sugar injection be brought about in depancreatized dogs; nor could any constant changes in this factor be produced by the pancreatic hormone of Knowlton and Starling.

S. B. S.

Blood-Dissociation Curves in Uræmia. EDWARD P. POULTON and JOHN H. RYFFEL (*Proc. physiol. Soc.*, 1913, xlvii—xlviii; *J. Physiol.*, 46).—Four cases of uræmia were investigated; the alveolar carbon dioxide pressure is low (14 to 25 instead of 40 mm.), and the blood takes up oxygen with difficulty, so that the percentage saturation is from 37 to 43 instead of 52 to 63. The lactic acid of the blood was not increased except in one case. The urea in the blood was high in all (0.21 to 0.36 instead of 0.03%). The meionexy is not due to the urea; addition of urea to normal blood does not cause the shifting of the curve.

W. D. H.

The Influence of Hydroxyl and Carboxyl Groups on the Pharmacological Action of Nitric Esters. CHARLES R. MARSHALL (*Eighth Inter. Cong. App. Chem.*, 1912, 19, 211—215).—The experiments were carried out on cats and rabbits with the following

substances: glycerol dinitrate, glyceryl methyl ether dinitrate, mannitol tetramethyl ether dinitrate, mannitol dimethyl ether etranitrate, mannitol pentanitrate, dulcitol pentanitrate, and the nitric esters of tartaric, citric, and lactic acids, and of their ethyl ethers. It was found generally that the presence of hydroxyl or methoxyl groups considerably diminishes the vaso-dilating action of the nitric esters. When compared with completely nitrated alcohols containing the same number of nitro-groups, most (but not all) of the esters containing hydroxyl or methoxyl groups are much less active. Carboxyl groups diminish the vaso-dilating power even more than these, and the nitric esters of tartaric, citric, and lactic acids, after neutralisation with sodium carbonate, were completely inactive as vaso-dilators.

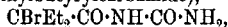
S. B. S.

The Biological Behaviour of 6-Chloro *m*-hydroxytoluic Acid.

ERNST SIEBURG (*Biochem. Zeitsch.*, 1913, 53, 259—264).—The substance investigated [Me: OH: CO₂H: Cl=1: 3: 4: 6] acts antiseptically about six times more strongly than phenol, and thirty times more strongly than sodium salicylate. Kobert's method was employed, in which milk is mixed with sulphur, and the concentration of the drug just necessary to inhibit hydrogen sulphide formation was ascertained. Its antiseptic power was also confirmed when pure cultures in sterile human urine were employed. When administered to man, the acid is relatively non-toxic, and 2 grams can be tolerated when administered in one dose, without evil effects. It is excreted in the form of the sulphuric acid ester, which is crystalline, melts and decomposes above 200°, and can be synthetically prepared by Baumann's method, the synthetical substance and the substance isolated from urine after ingestion of the acid being identical. The acetyl ester is readily hydrolysed by ferments contained in beer-yeast, trypsin, taka-diatase, rabbit's pancreas, and rabbit's liver.

S. B. S.

[Pharmacological] Investigation of Two Bromo-substituted Acidylcarbamides: Bromural and Adaline. Y. ARIELA (*Chem. Zentr.*, 1913, i, 2055; from *Skand. Arch. Physiol.*, 1913, 28, 193—277).—The pharmacological behaviour of bromural (monobromoisovalerylcarbamide), CHMe₂·CHBr·CO·NH·CO·NH₂, and of adaline (α -bromo- α -ethylbutyrylcarbamide),



has been investigated. In rabbits both behave similarly, adaline being the more lethal; they cause a diminution in the blood pressure, but are without effect on the heart.

E. F. A.

Action of Adrenaline on the Bronchioles. FREDERICK L. GOLLA and W. LEGGE SYMES (*Proc. physiol. Soc.*, 1913, xxxviii—xxxix; *J. Physiol.*, 46).—In cat and rabbit, adrenaline causes constriction of the bronchioles, but after constriction has been established by other drugs, such as curare or muscarine, adrenaline then causes dilatation. The following drugs resemble adrenaline in this particular: epinine (3: 4-dihydroxyphenyl-methylethylamine), tyramine (*p*-hydroxyphenylethylamine), methyl-

amine, ethylamine, and isoamylamine. Ergamine (β -amino-4-ethylglyoxaline) never produces bronchial dilatation.

W. D. H.

The Pharmacological Action of Bromostychnines. CHARLES R. MARSHALL (*Eighth Inter. Cong. App. Chem.*, 1912, 19, 217—223).—The two monobromostychnines act like strychnine, but are eight to nine times weaker. Dibromostychnine, although it still possesses a slight convulsant action in frogs and rabbits, produces in the former animals chiefly a paralytic effect, mainly due to a depression of the motor nerve-endings.

S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Favourable Action Exercised by Manganese on Acetic Fermentation. GABRIEL BERTRAND and ROBERT SAZERAC (*Compt. rend.*, 1913, 157, 149—151).—The addition of minute quantities of manganese has a marked accelerating influence on the conversion of alcohol into acetic acid by *B. aceti*. At first the acceleration increases with the proportion of manganese, then it reaches a maximum, and begins to decrease. Under the experimental conditions stated, 1 part of manganese sulphate in 10,000 had the optimum effect.

W. G.

The Production of Acetaldehyde During the Anaerobic Fermentations of Dextrose by *Bacillus coli communis* (Escherich). ECERTON CHARLES GREY (*Biochem. J.*, 1913, 7, 359—363).—By artificial selection of this bacillus by means of growth on sodium chloroacetate, strains have been obtained which produce little or no acetaldehyde. The formation of this product by the ordinary bacillus is related to the formation of alcohol, carbon dioxide, and hydrogen rather than to the other products. It is suggested that acetaldehyde is a primary product of the fermentation.

W. D. H.

Products of the Lactic Fermentation of Sugars. ALAN A. CLAPLIN (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 343—345).—There are considerable discrepancies between the statements of different authors with reference to the amount of lactic acid produced by the lactic fermentation of sugars, but the statement of Mayer and of Kayser is usually accepted, that the yield is not over 84%, and that considerable quantities of volatile acids are formed.

A further study of this question has shown that maltose, hydrolysed starch, and inverted sucrose give identical results when fermented with the same bacteria under the same conditions. It has been found that 95—97% of the sugar may be converted into

actic acid with formation of not more than 0.5% of volatile acids, the balance consisting of unfermented sugars. If all the sugar is fermented, the yield of lactic acid is reduced to 90%, and that of the volatile acids increased to 5%, the balance probably disappearing as water and carbon dioxide. The volatile acids are formic, acetic, propionic, and butyric acids, acetic and butyric being present in the largest quantities. The formic acid does not amount to more than 1% of the original sugar. The propionic acid occurs in the proportion of one part to ten parts of acetic acid. The percentage of acetic acid depends on the degree of aeration, and may attain as much as 30 parts to 70 parts of lactic acid. E. G.

Influence of Some Colloids on Alcoholic Fermentation. NICOLAAS L. SÖHNGEN (*Chem. Zentr.*, 1913, i, 2167—2168; from *Folia Microbiol., Holänd. Beitr. gesamt. Microbiol.*, 2).—Fermentation was affected between 38° and 40°, at which temperature the yeast no longer grows, but the fermentative function remains unchanged. The influence of a number of colloids on the process of alcoholic fermentation was investigated. Alkali humates have an adverse action. Colloidal iron, aluminium, or silicon oxides and humic acid have no measurable influence. Biocolloids, such as turf, blood-charcoal, garden soil, have a markedly favourable action. This is attributed to the low concentration of carbon dioxide in these liquids, which favours the rapid formation and dissipation of bubbles, so that the medium does not become supersaturated. The aggregation of the gas bubbles at the colloidal surfaces accelerates their liberation and escape. E. F. A.

Catalysts of Alcoholic Fermentation. HANS EULER and HENRY CASSEL (*Zeitsch. physiol. Chem.*, 1913, 86, 122—129).—Whilst most of the substances known to accelerate fermentation have a comparatively slight effect—the maximum rarely exceeding 20%—it was found that addition of 0.04 gram of ammonium formate to 110 c.c. of water and 2 grams of sucrose resulted in an increase of 75%. Dry yeast was scarcely, if at all, influenced by ammonium formate.

Further experiments showed that the addition of ammonium formate affects the first phase of fermentation, in which an intermediate product, or products, are formed, more than the second phase (production of alcohol and carbon dioxide).

The effect of a given amount of organic salt is greater the less yeast is present.

N. H. J. M.

Influence of the Yeasts and of the Initial Constitution of the Musts on the Acidity of Fermented Liquids. JULES VENTRE (*Compt. rend.*, 1913, 157, 154—156. Compare Fernbach, this vol., i, 231).—A study of the fermentation of sugar solutions by different yeasts in media of varying acidity, and of the effect of using different organic acids to produce the initial acidity. Each yeast produces a definite fixed and volatile acidity, the acidity increasing in neutral media, but diminishing in natural or artificial acid

media. Tartaric acid is preserved unchanged in original amount, but little being consumed by the different yeasts. Malic acid appears to be the most readily attacked by the yeasts. Each yeast has a power peculiar to itself of producing succinic acid. W. G.

Fermentations with Yeast in Absence of Sugar. XII. Changes During Fermentation by Yeast. CARL NEUBERG and JOHANNES KERB (*Ber.*, 1913, 46, 2225—2228; *Biochem. Zeitsch.*, 1913, 53, 406—419).—Pyruvic acid, $\text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H}$, is rapidly broken down by an enzyme in yeast into acetaldehyde and carbon dioxide (compare Neuberg and Kerb, A., 1912, ii, 973). The fermentation of a mixture of pyruvic acid and glycerol has been repeated on a large scale, using 100 litres of 1% pyruvic acid. Precautions were taken that the yeast had a high fermentative power, and allowance was made for the alcohol already present in the yeast used, and also for the alcohol formed by autofermentation. A considerable amount of alcohol is formed from pyruvic acid, and still more when both pyruvic acid and glycerol are present. It is considered that the influence of the glycerol is only indirect, in that it acts to protect the enzyme and increase its reducing power.

*iso*Butaldehyde and valeraldehyde are readily converted by yeast into the corresponding alcohols with a yield of 85% in the latter instance. E. F. A.

The Separation of Life and Fermentative Power. THOMAS BOKORNY (*Pflüger's Archiv*, 1913, 152, 365—436).—Experiments on yeast show that by chemical reagents of appropriate strength it is possible to kill the cells, but leave the enzymic power intact; for instance, this is accomplished by sulphuric acid from 0.1 to 0.5% concentration. Details regarding a large number of chemical reagents (inorganic and organic) are given. The kind of yeast used is one factor in the process. W. D. H.

The Fat of Yeast. H. A. D. NEVILLE (*Biochem. J.*, 1913, 7, 341—348).—The chief saturated acid in the fat of yeast is penta-decoic acid (Hinsberg and Roos, A., 1903, i, 56); arachidic acid and unsaturated acids with the formulæ $\text{C}_{16}\text{H}_{32}\text{O}_4$, $\text{C}_{18}\text{H}_{34}\text{O}_2$, and $\text{C}_{18}\text{H}_{32}\text{O}_2$ are also present. The cholesterol melts at 145—147°. W. D. H.

The Protein Substances of Yeast and their Products of Hydrolysis. PIERRE THOMAS and (Mme.) SOPHIE KOLODZIESKA (*Compt. rend.*, 1913, 157, 243—246. Compare this vol., i, 942).—The authors have studied the products of hydrolysis of the two protein substances obtained from yeast (compare *loc. cit.*), one of which belongs to the casein group, and the other to the vegetable albumins. By hydrolysis with concentrated hydrochloric acid, followed by distillation with magnesium oxide, and then precipitation of the humic nitrogen by evaporation in acid solution, and of the amino-compounds with phosphotungstic acid, the nitrogen content has been determined as ammoniacal, humic, diamino- and

monamino-nitrogen. The figures are in fairly close agreement with Osborne's values for casein. Similar treatment of the cerevisine or vegetable albumin gives values agreeing well with Osborne's results for legumeline.

Hydrolyses have also been performed with sulphuric acid, and estimations made of the histidine, arginine, and lysine. W. G.

A Forgotten Investigator. A Contribution to the History of the Yeast Manufacture. F. G. WALLER (*Chem. Weekblad*, 1913, 10, 635—644).—A review of the development of the manufacture of yeast, in which the author contends that a practical technical method for its production by the air process was first devised by Eusebius Bruun. A. J. W.

Potassium, Sulphur, and Magnesium in the Metabolism of *Aspergillus niger*. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1349—1355).—Deficiency of potassium chloride allows the production of mycelium, but not of spore formation. Only in the concentration of $M/37,500$ does spore formation commence after eight days. When potassium sulphate is added, larger quantities inhibit the formation of spore, which develop after two days, when potassium sulphate is absent. After forty days, all the moulds were covered with spores in all the concentrations of sulphate added. During the growth, sulphur accumulates in the cells, and is afterwards partly excreted. Relatively large quantities of magnesium are necessary to produce a perceptible growth of mycelium, as none visible to the naked eye appeared even in the concentration of $M/2,470,000\text{-MgSO}_4 \cdot 7\text{H}_2\text{O}$ per litre. In the concentration $2M/247,000$, considerable growth only appeared after some days. S. B. S.

Amygdalase and Amygdalinase in *Aspergillus niger* and Some Allied Hyphomycetes. MAURICE JAVILLIER and (Mme.) HELENE TSCHERNORUTZKY (*Ann. Inst. Pasteur*, 1913, 27, 440—449).—*Sterigmatocystis nigra* and most of the mosses examined contain unequal amounts of amygdalase and amygdalinase. The amounts of both diastases is diminished in absence of zinc. The diastases are active in solutions which are neutral or slightly acid to helianthin, and the optimum temperature is higher than that of the same diastases of almonds.

The percentage amount of the diastases in the plants varies with the age of the mycelium, and reaches its maximum at the time of sporulation. The two diastases pass into the culture medium very unequally.

N. H. J. M.

Biological and Toxicological Studies on *Penicillium stoloniferum* (Thom.). CARL L. ALSBERG and OTIS F. BLACK (*Eighth Inter. Cong. App. Chem.*, 1912, 19, 15—23).—Cultures of *Penicillium stoloniferum* were obtained by Thom from spoiled Italian maize. When grown on Ranlin's medium, these were found to produce an acid, $\text{C}_{17}\text{H}_{20}\text{O}_6$, white needles, m. p. 140° , which was of phenolic character, almost insoluble in water, but soluble in

most organic solvents, to which the name *mycophenolic acid* is given. It gives with ferric chloride the colour which is characteristic of spoiled Italian maize, and resembles in many respects the lichen acids.

S. B. S.

Sterigmatocystis nigra and Lactose. HENRI BIERRY and (Mlle.) F. COUPIN (*Compt. rend.*, 1913, 157, 246—247).—By cultivation of *Sterigmatocystis nigra* on Raulin's liquid for three days, then on a similar liquid deprived of all carbohydrate, and finally on this liquid with the sucrose replaced by lactose, lactase is produced in the plant, but in an endocellular form, and in consequence it does not pass into water when the crop is macerated with it.

W. G.

The Influence of the Chemical Constitution of Certain Organic Hydroxyl and Aminic Derivatives on their Germicidal Power. GILBERT T. MORGAN and E. ASHLEY COOPER (*Eighth Inter. Cong. App. Chem.*, 1912, 19, 243—257).—The antiseptic value of several series of substances was investigated by Chick and Martin's modification of the Rideal-Walker process. The antiseptic value of the following classes of substances was ascertained. The aliphatic alcohols: The "carbolic acid coefficients" of these were all low. Certain phenols: The influence of the addition of alcohol to these was also investigated, and found to vary in different cases. The carbolic acid coefficients of the dihydroxybenzenes were as follows. (With *B. Typhosus*) Resorcinol, 0.29; catechol, 0.48; quinol, 1.1. The results with the nitrophenols were as follows (*Staphylococcus py. aur.*): *p*-Nitrophenol, 2.3; potassium *p*-nitrophenoxide, 0.52; *m*-nitrophenol, 3.5; picric acid, 7.5. The coefficients for coumarin, the coumaric acids and salts were low. The coefficients for the dihydroxynaphthalenes were, for the 2:3-derivative, 4.4, and for the 2:7-derivative, 2.8. The coefficients of several series of both aliphatic and aromatic amines were also determined. The chief results are the following (with *B. Typhosus*), ethylamine, 1.27; isoamylamine, 2.8; *n*-heptylamine, 24.3; *ac*-tetrahydro- β -naphthylamine, 5.3; aniline, 0.57; the toluidines, ortho-, 1.00; meta-, 1.30; para-, 1.25; pyridine, 0.18.

S. B. S.

Compounds Obtained from Plant Seeds by the Methods for Extracting Lecithin. I. Introduction: Bean Seeds. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1913, 86, 1—32).—A summary is given of previous work on plant phosphatides, and the opinion is expressed that the apparent differences between plant and animal phosphatides is due to the incomplete investigation of the former and to incorrect interpretation of the experimental results. The preparation and purification of the lecithin contained in *Phaseolus vulgaris* is described.

E. F. A.

Compounds Obtained from Plant Seeds by the Methods for Extracting Lecithin. II. Hydrolysis of Egg-albumin. III. Oat Seeds. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1913, 86, 141—152, 153—173).—Previous experiments having shown that

aminoethyl alcohol is obtained by hydrolysing the lecithin of bean seeds, it became desirable to ascertain whether the compound could be obtained from other lecithins. Egg-lecithin, when hydrolysed, yielded, in addition to choline, small amounts of aminoethyl alcohol and glycerolphosphoric acid. Evidence was obtained that the aminoethyl alcohol is attached to the lecithin by the hydroxyl group, the amino-group being free.

Further experiments, with oats, showed that the phosphatides of the seeds of cereals are very similar to egg-lecithin and the lecithins of leguminous seeds.

N. H. J. M.

Quantitative Experiments on the Effect of Formaldehyde on Living Plants. SARAH M. BAKER (*Ann. Bot.*, 1913, 27, 411—442).—The results of experiments on the growth of seeds in atmospheres containing known amounts of formaldehyde showed that in presence of light, formaldehyde is utilised to some extent for the synthesis of food materials. In absence of light, formaldehyde is not assimilated; it seemed, however, to stimulate respiration.

Acetaldehyde is not assimilated in presence of light. The change in the dry weight of the cultures, when compared with the carbon dioxide respired, gave a ratio closely agreeing with that calculated for the complete oxidation of a carbohydrate. With cultures kept in darkness, no change occurred in the relations between loss in dry weight and the respired carbon dioxide. Formaldehyde was therefore not converted into carbon dioxide, and was not used as a source of food materials in absence of light.

It is probable that formaldehyde may function as a stage in photosynthesis; but the production of sugars and other food materials requires light energy.

N. H. J. M.

Action of Sulphites, Thiosulphates, and Sulphur in Soils on the Growth of Plants. WALTER THALAU (*Landw. Versuchs-Stat.*, 1913, 82, 161—209).—The results of pot experiments with different plants showed that, in a loamy soil, ammonium sulphite has the same effect as ammonium sulphate; in sand, ammonium sulphite has somewhat less effect than the sulphate; whilst in peat the yield was much less with sulphite.

In water cultures, ammonium sulphite is very injurious; germination is retarded in 0.4% solutions.

When exposed to air for a short time, ammonium sulphite is oxidised to sulphate; the rate of oxidation is increased by dissolving the salt in water, and still more in presence of soil.

Calcium sulphite was found to have no injurious action in loamy and sandy soils; in water cultures, and perhaps in peat, it reduced the yields. Sodium thiosulphate had no injurious effect. Flowers of sulphur had no very appreciable effect, and further experiments will be necessary.

N. H. J. M.

Presence of Hemicelluloses in Root-stock, Rhizomes, and Tubers. ANTON STIEGER (*Zeitsch. physiol. Chem.*, 1913, 86, 270—282).—The investigation of root-material from a number of

plants showed that in every case hemicellulose was present, a mixture of galactose and arabinose in approximately equal quantities being obtained on hydrolysis, whilst in no instance was either mannose or fructose present. The root and rhizome of *Asparagus officinalis* yielded only arabinose. The presence of much or little starch in the roots had no apparent effect. It is left undecided whether the hemicelluloses act as a reserve or as a skeletal material in the vegetative parts of plants. E. F. A.

Distribution of Asparagine, Glutamine, Arginine, and Allantoin in Plants. ANTON STIEGER (*Zeitsch. physiol. Chem.*, 1913, **86**, 245—269).—Asparagine and glutamine were sought for in the roots, underground shoots, portions above ground, or in the seedlings of a large variety of plants. It is characteristic of some families that they contain asparagine alone; in others only glutamine is present, whilst a few contain both amides. The last may contain either amide in excess or both in equal proportions. The results show a remarkable parallelism between the morphological-anatomical classification of the plants and their chemical behaviour. Certain irregularities are recorded where plants, in which normally only asparagine is present, sometimes contain more or less glutamine as well. Such variations are attributed to the altered conditions of environment.

Arginine almost always accompanies asparagine, but is less often present with glutamine. It is found when neither amide is present, where it probably acts as a reserve material.

The presence of allantoin in a number of plants is established.

E. F. A.

Antiaris Latex. HEINRICH KILIANI (*Ber.*, 1913, **46**, 2179—2188. Compare this vol., i, 381).—A fresh supply of preserved Antiaris latex was received from Mid-Borneo. It contained a deposit of the protein in the form of well-defined, short columns. The latex is therefore a saturated solution of the protein, which must be an original ingredient, and not the product of subsequent fermentation. On this occasion, the most exhaustive extraction, full details of which are described, failed to yield more than one-sixth of the amount of glucosides which was previously obtained, and only β -antiarin (0.1% of the latex), but no α -antiarin could be isolated. The crude glucoside contained, however, a new active substance, which is easily soluble in water, and is designated γ -antiarin.

Ether extracted from the alcoholic solution of the glucosides a new acid, $C_{16}H_{14}O_7$ (?), which forms pale yellow, glistening crystals, sinters at 178—184°, is strongly acid, gives a calcium salt, and develops a green coloration with ferric chloride, changing to deep red with a drop of ammonia. The alkaline solutions rapidly darken in the air, from which it appears that the acid is a pyrogallol derivative, probably metamerie with lecanoric acid.

J. C. W.

Alcohol From the Fruit of *Arbutus unedo* (Ellerone).
GIOVANNI SANI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 884—885).—Fermentation of this fruit yields a product containing 9.15—9.75% of alcohol. The alcohol recovered from it by distillation had an acidity of 0.132 gram per litre (as acetic acid), contained esters (1.757 grams per litre, as ethyl acetate), furfuraldehyde, methyl alcohol, and fusel oil (2.321 grams per litre), but no free or combined hydrogen cyanide.
R. V. S.

Chemical Examination of the Seeds of the Cacao Tree.
L. REUTTER (*Compt. rend.*, 1913, 156, 1842—1844).—Ground cocoa beans were treated with steam at 110°, deprived of oil, and extracted with warm dilute methyl alcohol. On spontaneous evaporation, the reddish-violet solution deposits white, microscopic crystals, m. p. 184—185°. This substance, termed *cacaorine*, $C_{16}H_{20}O_5N_3$, yields a neutral solution in water, which is optically inactive. On hydrolysis, it yields theobromine and a small quantity of a reddish-brown precipitate.

The mother liquor from *cacaorine*, when further concentrated, yields *cacao-red*, $C_{40}H_{60}O_{27}N$, reddish-violet leaflets, which slowly oxidise on exposure to air, becoming brown. It is soluble in water and in methyl alcohol. The aqueous solution is coloured yellowish-brown by alkalis, bright red by acids. It reduces Fehling's solution, but is optically inactive. When hydrolysed by dilute sulphuric acid, it yields carbon dioxide, a dextrorotatory sugar, and *cacao-brown*, $C_{76}H_{18}O_{34}N$.
H. W.

Ash of the Castor Bean. MARSTON LOVELL HAMLIN (*Biochem. Bull.*, 1913, 2, 410—411).—The following were the results obtained:

	SiO ₂	CaO	MgO	P ₂ O ₅	Mn	Total ash.
Per cent. in dry oil-free kernel...	0.04	0.28	1.51	3.52	0.00056	7.3
Per cent. in ash	0.5	3.9	20.7	48.2	0.0076	—

Schulze and Godet obtained the following figures from dry, but not oil-free, kernels:

	CaO	MgO	P ₂ O ₅	Total ash.
Per cent. in dry substance ...	0.15	0.72	1.16	3.64
Per cent. in ash	4.0	19.8	31.9	—

W. D. H.

The Composition of Coffee Essence; Presence of Pyridine.
GABRIEL BERTRAND and GUSTAVE WEISWEILLER (*Compt. rend.*, 1913, 157, 212—213).—The authors have proved the presence of pyridine in the infusion of freshly roasted and ground coffee, by precipitation with silicotungstic acid and subsequent preparation of its platinum-chloride. Pyridine is present to the extent of 200—250 mg. per kilo. of freshly roasted coffee.
W. G.

Nitrogenous Constituents of the Fungus, *Cortinellus shiitake* (P. Henn.). KIYOHISA YOSHIMURA and M. KANAI (*Zeitsch. physiol. Chem.*, 1913, 86, 178—184).—The sample examined contained 37.355% of dry matter of the following composition:

Nitrogen.			Crude fat.	Ash.	P ₂ O ₅ .
Total.	As proteins.	As ammonia.			
3.993	2.406	0.085	0.641	5.781	0.804

The following substances were obtained from 2 kilos. of the air-dried fungus: adenine, 0.40; choline, 0.41; alanine, 1.60; leucine, 2.30; copper glutamate, 0.50; proline, 0.30; mannitol, 50.00 grams; also a trace of trimethylamine and a little phenylalanine.

N. H. J. M.

Latex of *Ficus coronata*; an Incomplete Vegetable Pancreatic Juice Containing a Proteolytic Enzyme, but no Amylase. C. GERBER (*Compt. rend.*, 1913, 156, 1917—1919. Compare A., 1911, ii, 647; 1912, ii, 801, 977).—The latex has no action on starch paste or soluble starch, and consequently contains no amylase. Judging from its action on egg-yolk, it contains a lipase twice as active as that in the latex of *Ficus carica* (*loc. cit.*), and slightly more resistant to the influence of heat and of acids. It also contains a very active proteolytic ferment, which from its activity in coagulating milk appears to be four times as active as the similar ferment in *Ficus carica* latex, and more resistant to heat than the latter. The rennet of *Ficus coronata* is affected by acids and salts in the same way as that of *Ficus carica*. The latex is like that of *Morus nigra*, an incomplete vegetable pancreatic juice, but differs from this in containing a rennet more active towards boiled than raw milk.

T. A. H.

The Influence of the Carbonates of the Rare Earths (Cerium, Lanthanum, Yttrium) on Growth and Cell Division in Hyacinths. WILLIAM HOWEL EVANS (*Biochem. J.*, 1913, 7, 349—355).—The concentration of the carbonates of the rare earths necessary to produce physiological effects is very small. Lanthanum and cerium are favourable to growth and cell-division; yttrium is unfavourable. The lanthanum ion has a special effect on the flower-stalk, causing an increase in length.

W. D. H.

Value of Caoutchouc in *Kickxia-elastic*. DAVID SPENCE and WILLIAM F. RUSSELL (*Kolloid. Zeitsch.*, 1913, 13, 41—46).—The authors have worked up six specimens of indiarubber latex by different methods with the object of ascertaining whether the kickxia caoutchouc could be converted into a good commercial product. They conclude that when carefully worked, this substance, as far as its physical properties are concerned, gives a good caoutchouc, but as far as its composition and other properties are concerned, the kickxia latex is inferior to the Plantagen-Hevea latex.

J. F. S.

Analyses of Some Wyoming Larkspurs. I. FREDERICK W. HEYL, F. E. HEPNER, and SYLVESTER K. LOY (*J. Amer. Chem. Soc.*, 1913, 35, 880—885).—Analyses are given of the various parts of *Delphinium Nelsonii*, *Delphinium glaucum*, and *Delphinium geyeri*.

The leaves of all three varieties were found to contain *d*-mannitol, whilst the last variety is found to yield the highest proportion of mixed alkaloids. D. F. T.

Constituents of the Berries of Kuko (*Lycium chinense*). T. FURUYA (*Chem. Zentr.*, 1913, i, 1823; from *Arb. Pharm. Inst. Univ. Berlin*, 9, 117—120).—The berries of Kuko (*Lycium chinense*) yield 0.0912% of betaine. E. F. A.

Constituents of the Roots of *Stemona sessilifolia*. T. FURUYA (*Chem. Zentr.*, 1913, i, 1823—1824; from *Arb. Pharm. Inst. Univ. Berlin*, 9, 112—116).—The powdered roots contain an alkaloid *hodorine*, $C_{19}H_{31}O_6N$, which was not obtained crystalline. The *hydrobromide* forms a colourless, odourless, crystalline powder, m. p. 258—259°. The *hydrochloride* has m. p. 244—247° (decomp.). E. F. A.

Manketti Seed Oil. HERMANN THOMS (*Chem. Zentr.*, 1913, i, 1823; from *Arb. Pharm. Inst. Univ. Berlin*, 9, 225—227).—Manketti seeds yield a pale yellow oil of nutty odour and agreeable flavour. The oil becomes cloudy at -2° . It is optically inactive, and has the following constants: Saponification number, 195.2; Reichert-Meissl, 1.085; Polenske, 0.6; iodine number, 130.4; Hehner number, 98.5; m. p. of the fatty acids, 40° ; iodine number of these, 140.7; acetyl number, 163.2. The crude oil consists of the above oil, a half solid fat, m. p. 33° , and a watery fluid. E. F. A.

"Tannin Masses" in the Persimmon Fruit. ERNEST D. CLARK (*Biochem. Bull.*, 1913, 2, 412—418).—On hydrolysis of tannin masses from the persimmon, tannin, phloroglucinol, and much colloidal residue are obtained, but no hexose or pentose. The union between the two first-mentioned substances is probably similar to that of phloroglucintannoids in various plants. The colloidal residue is cellulose-like. In the presence of phloroglucinol, the ferric chloride test for tannin is untrustworthy. W. D. H.

Investigation of *Puccinia graminis* Persoon. A. VON POMARSKI (*Chem. Zentr.*, 1913, ii, 288; from *Sep. Zoot. Lab.*, 1912, 8, 85—120).—The air-dried spores of *Puccinia graminis* contain 12.1% of moisture, 3.25% of nitrogen, 5.1% of fat, and 9.15% of cell membrane. The last yields dextrose, formic and acetic acids on hydrolysis, it contains about 7% of nitrogen, and is analogous to chitin or chitosan.

The fat contains lauric acid, heptolic acid, oleic acid, and glycerol, also 32% of a wax and dioleincithin.

Dextrose, mannitol, and an unknown disaccharide are present, also the enzymes, invertase, catalase, diastase and lipase, as well as brownish-red and green pigments. E. F. A.

Arsenic and Manganese in Some Seaweeds. HENRI MARCELET (*Chem. Zentr.*, 1913, ii, 278; from *Bull. Sci. Pharmacol.*, 1913, 20, 271—275).—Seaweeds contain from 0.005 to 0.5 mg. of

arsenic per 100 grams of dry material. Apparently the proportion of arsenic is greatest when that of chlorophyll is least; this is the opposite of the relation in land plants. In *Posidonia* the leaves contain 0.045 mg.; the roots, 0.035 mg.; and the whole plant, 0.04 mg. of arsenic per 100 grams.

E. F. A.

***Occurrence of Trehalose in *Selaginella lepidophylla*.** OTTO ANSELMINO and E. GILG (*Ber. deut. Pharm. Ges.*, 1913, 23, 326—330).—On extraction with alcohol, *Selaginella lepidophylla* furnished trehalose, which was identified by means of its melting point, composition, etc. *S. Galeottii* and *S. Kraussiana* yielded no trehalose.

T. A. H.

The Unsaponifiable Constituents of Sesame Oil. ALFRED HEIDUSCHKA (*Eighth Inter. Cong. App. Chem.*, 1912, 11, 13—16).—Sesame oil contains three unsaponifiable substances, namely, phytosterol, sesamin, and a thick yellow oil. The phytosterol, m. p. 136.2—136.8°, is a definite compound, and cannot be separated, by fractional crystallisations, into fractions having different melting points. Sesame oil yields about 0.17% of sesamin; this contains 67.36% of carbon and 5.43% of hydrogen, and has a molecular weight of 341.8. From these figures the formula $C_{20}H_{19}O_6$ is deduced for the substance. The yellow oil could not be separated into any characteristic or definite substances.

W. P. S.

Chemical Examination of Wheat Germ. FREDERICK B. POWER and ARTHUR H. SALWAY (*Pharm. J.*, 1913, 91, 117—120).—Wheat germ was found to contain sitosterol, choline, betaine, allantoin, sucrose, dextrose, and raffinose; no evidence was obtained of the presence of asparagine, which has been recorded as a constituent of wheat germ by Frankfurt (A., 1897, ii, 67). About 7% of fatty oil was obtained from the wheat germ under examination, the oil consisting of the glycerides of stearic, palmitic, and linolic acids; the quantity of linolic acid was about three times as much as that of the total solid acids. The amount of resinous substance present was 0.04%, as was also a small quantity of an amorphous glucosidic substance. It was ascertained that wheat germ contains a very small amount of sinapic acid, probably present as sinapine, a choline ester of sinapic acid.

W. P. S.

Influence of the Lime-Magnesia Ratio. P. L. GILE and C. N. AGERTON (*J. Ind. Eng. Chem.*, 1913, 5, 564—567).—Experiments are described in which bush beans were grown for three years on plots 30 × 60 dcm., the soil of which contained varying proportions of lime and magnesia.

The results indicate that bush beans are independent of lime-magnesia ratio in the soils employed; and that the amount of lime in the plants remained the same, with increasing amounts of lime in the soil.

The conclusion is drawn that whilst the ratios of different salts,

including lime and magnesia, affect plant growth under certain conditions, the hypothesis of the lime-magnesia ratio cannot be considered as applying to all soil conditions. N. H. J. M.

Unfermentable Sugar (Pentose) and the Formation of Furfuraldehyde in Wine. RUDOLF HAID (*Chem. Zentr.*, 1913, i, 2170; from *Zeitsch. Gärungsphysiol.*, 1913, 2, 107—109. Compare Pasquero and Cappa, A., 1912, ii, 103).—The furfuraldehyde formed on the distillation of wine cannot be derived from *L*-arabinose, since this pentose, when distilled with malic or tartaric acid, does not yield furfuraldehyde. An unknown pentose is assumed to be the source of the aldehyde. E. F. A.

The Advance and Prospects of the Newer Agricultural Chemistry (Chiefly Land Chemistry) since the Discoveries of Modern Physical Chemistry and Colloidal Chemistry Have been Employed. HANS BREHM (*Kolloid. Zeitsch.*, 1913, 13, 19—35).—The author considers the work which has been done in connexion with agricultural soil and the processes taking place in it, from the colloidal chemistry point of view. The various substances occurring in the soil are individually considered, and a long bibliography of the chief researches on the subject from 1901 to the present time is given. J. F. S.

Mineralogical Soil Analysis. WILLIAM J. MCCAUGHEY (*J. Ind. Eng. Chem.*, 1913, 5, 562—564).—The potassium minerals usually present in soils are orthoclase, microcline, muscovite, and biotite. Muscovite is the most resistant, and probably contributes very little to the soil solution; biotite is the most readily decomposed. Orthoclase is the commonest, and occurs in amounts varying from 3 to 30%.

The commonest calcium minerals are epidote, hornblende, plagioclase, and garnet. Epidote is a normal constituent of most soils, whilst garnet, which is formed by contact metamorphism, occurs less frequently. Hornblende is the common calcium mineral, and weathers generally, forming chlorite.

Quartz crystals occur so frequently in limestone soils and are so exceptional in others, that their presence seems to indicate origin from limestone. N. H. J. M.

Quantitative Investigations on the Reaction of Aqueous Extracts of Soils. TEODOR SAIDEL (*Bull. Acad. Sci. Roumaine.*, 1913, 2, 38—44).—An electrical method for estimating the reaction of soil extracts is described with sketch of the apparatus employed. The difficulty due to loss of carbon dioxide when hydrogen is passed through the solution can be overcome by mixing the hydrogen with a definite amount of carbon dioxide, or else by boiling off the carbon dioxide.

The results of estimations obtained with several soils shows that there is a considerable difference in reaction between forest soils and the soils of the steppes on the one hand, and podsol soils on the other. N. H. J. M.

Alkaline Reactions Caused by Acids and their Acid Salts in Soils. GIULIO MASONI (*Chem. Zentr.*, 1913, i, 1999; from *Staz. speriment. agrar. ital.*, 1912, 46, 219—240. Compare A., 1912, ii, 677).—Organic and mineral acids and their acid salts are able to cause an alkaline reaction in soils. In calciferous soils, calcium carbonate is formed, which in aqueous solution, on the addition of acid, parts with hydroxyl. The alkaline reaction may also be due to the action of acids on basic salts of magnesium, calcium, or aluminium. Acid alkali salts will give rise to alkali carbonates. The influence of the alkaline reaction on the biological function of the roots is discussed.
E. F. A.

Behaviour of Amino-acids in the Soil. SAMUEL L. JORDI (*Eighth Inter. Cong. App. Chem.*, 1912, 26, 119—134. Compare A., 1911, ii, 820; 1912, ii, 292).—In connexion with a study of the proteins contained in soils, experiments have been undertaken to ascertain the rate at which amino-acids in the soil eliminate their nitrogen in the form of ammonia and whether the process is quantitative. In these experiments, definite quantities of various amino-acids were mixed thoroughly with weighed portions of soil and kept in covered vessels at 22—27°; after the lapse of some days the quantity of ammoniacal nitrogen formed was estimated. The various amino-acids yielded under these conditions the following maximum proportions of ammonia: glycine, 81.03%; alanine, 75.58%; leucine, 59.62%; aspartic acid, 72.74%; glutamic acid, 72.19%; phenylalanine, 54.31% tyrosine, 59.65% asparagine, 77.47%.

The results do not show whether amino-acids can be quantitatively de-aminated in the soil. It is possible that during the course of the process, some of the ammonia produced is oxidised to nitrites and nitrates. There are also other factors to be taken into consideration. It has been demonstrated, however, that the amino-acids examined readily lose nitrogen in the form of ammonia, and that the rate of the change is greatly influenced by the structure of the acids, acids of similar structure yielding about the same proportion of ammonia.
E. G.

Normal and Abnormal Constituents of Soil Organic Matter. ELBERT C. LATHROP (*Eighth Inter. Cong. App. Chem.*, 1912, 15, 147—151).—The following compounds may be considered as normally present in soils: pentosans, histidine, xanthine, hypoxanthine, cytosine, and, perhaps, creatinine. Arginine and adenine only occur infrequently, whilst dihydroxystearic and picolinic-carboxylic acids, being injurious to plants, must be classed as abnormal soil constituents.

It is uncertain whether agroceric, lignoceric, paraffinic and mono-hydroxystearic acids, agosterol, phytosterol, and hentriacontane should be considered as normal or abnormal constituents of soils.
N. H. J. M.

Organic Chemistry.

Determination of the Critical Constants of Methane. ETTORÉ CARDOSO (*Arch. Sci. phys. nat.*, 1913, [iv], 36, 97—100).—Preliminary details are given of the apparatus employed in the determination of critical constants; the following values are found for methane: critical temperature, 82·85°; critical pressure, 45·60 atm.; critical density, 0·1623. J. F. S.

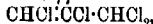
Preparation of Erythrene and Isoprene. FARBENFABRIKEN FORM. FRIEDR. BAYER & Co. (D.R.-P. 261876).—When the hydrochlorides of δ -dimethylamino- Δ^2 -isoamylene and of δ -dimethylamino- Δ^2 -butylene (this vol., i, 342) are heated at 200—240°, they decompose into dimethylamine and isoprene or erythrene respectively. F. M. G. M.

Preparation of Halogenated Propanes. HENDRIK JACOBUS PRINS (D.R.-P. 261689).—Compounds of general formulæ C_3X_5H , $C_3X_4H_2$ and $C_3X_3H_3$ (where X is Cl or Br), are readily prepared from a mixture of halogenated methane and halogenated ethylenes (of formulæ CX_2 :CHX and CHX:CHX) by mixing together in the required proportions in the presence of aluminium chloride or bromide at about 20°.

aa β yy-Hexachloropropane, $CCl_3\cdot CHCl\cdot CHCl_2$, obtained from chloroform (or carbon tetrachloride) and dichloroethylene, is a colourless liquid, b. p. 216°; when treated with alcoholic potassium hydroxide at the ordinary temperature, it gives rise to *aa β yy-pentachloropropylene*, $CCl_3\cdot CCl\cdot CHCl_2$, b. p. 184°, from which *a β β -trichloroacetaldehyde*, $CCl_3\cdot CCl\cdot CHO$, b. p. 164°, is obtained by the action of concentrated sulphuric acid, which latter can further be converted into *a β -dichloroacrylic acid*, $CHCl\cdot CCl\cdot CO_2H$, and its *amide*, $CHCl\cdot CCl\cdot CO\cdot NH_2$, m. p. 132°.

aa β yyy-Heptachloropropane, $CCl_3\cdot CHCl\cdot CCl_3$, is an oil with a penetrating odour, m. p. 11—12°, b. p. 164—166°/90 mm., $D_4^{15} 1\cdot 9$, $n_D^{15} 1\cdot 5418$, and in a similar manner furnishes *hexachloropropylene*, C_2Cl_6 , b. p. 210°, and *trichloroacrylic acid*.

aa β yy-Pentachloropropane, $CHCl_2\cdot CHCl\cdot CHCl_2$, a colourless liquid, b. p. 198—200°, gives rise to *a β yy-tetrachloropropylene*,



b. p. 165°, and the *aldehyde*, $OH\cdot CH\cdot CCl\cdot CHO$, m. p. 145°.

aa β yy-Pentabromopropane, $CHBr_2\cdot CHBr\cdot CHBr_2$, has b. p. 163—165°/18 mm.

F. M. G. M.

Catalytic Action of Certain Manganese Salts on Alcohols (Spirits) in the Presence of Hydrogen Peroxide. A. C. CHAUVIN (*Ann. Patisif.*, 1913, 6, 463—466).—The addition of 1% of hydrogen peroxide solution (perhydrol) to crude alcohol, spirits, and liqueurs, produces, after thirty days' contact, an increase in the quantities of the usual impurities (aldehydes, esters, higher alcohols, etc.), which were

present originally, but the furfuraldehyde tends to disappear. The action of the peroxide is augmented by the addition of about 0.01% of manganese salts, the acetate having the greatest effect. In the case of kirsch liqueur the hydrocyanic acid is decomposed by the treatment, whilst the essential oils present in absinthe are resinified. W. P. S.

Preparation of Esters from Alcohols and Organic Acids. OTTO HAUSER and ADOLF KLOTZ (D.R.-P. 261878).—An account of work previously described (Hauser and Klotz, this vol., i, 246). *tert. Butyl n-nonoate* has b. p. 242° , and *tert.-butyl n-octoate*, b. p. 231° .
F. M. G. M.

Alkylation of Ethyl Cyanoacetate. JOHN C. HESSLER (*J. Amer. Chem. Soc.*, 1913, 35, 990—994).—The ethylation of ethyl cyanoacetate has already been studied (Hessler, A., 1908, i, 182; 1904, i, 830; Hadley, A., 1912, i, 699), and the author has now turned his attention to the substitution of other alkyl groups into this ester.

Crude ethyl α -cyanopropionate, obtained by the action of sodium ethoxide and methyl iodide on an alcoholic solution of ethyl cyanoacetate (Henry, A., 1887, 796), after shaking with 10% sodium hydroxide solution and subsequent fractionation yielded about 12% of ethyl α -cyano- α -methylpropionate, b. p. $77^{\circ}/9$ mm., $185^{\circ}/\text{ord. pressure}$, D_{20}^{20} 0.971. The sodium hydroxide extract contained α -cyanopropionic acid, b. p. 142 — $145^{\circ}/11$ mm., D_{20}^{20} 1.14, from the silver salt of which pure ethyl α -cyanopropionate, b. p. 89 — $90^{\circ}/20$ mm., 192 — $193^{\circ}/\text{ord. pressure}$, D_{22}^{22} 0.998, was obtainable by the action of ethyl iodide.

Crude ethyl α -cyanoisovalerate, prepared in a similar manner to the above methyl derivative, was submitted to like treatment with sodium hydroxide; it yielded about 10% of ethyl α -cyano- α -isopropylisovalerate, b. p. 240° , $D_{29.4}^{29.4}$ 0.918, and also cyanoisovaleric acid, b. p. 166 — $168^{\circ}/28$ mm.; the silver salt of the latter reacted vigorously with ethyl iodide, giving pure ethyl α -cyanoisovalerate, b. p. $113^{\circ}/25$ mm., $211^{\circ}/739$ mm., $D_{29.2}^{29.2}$ 0.962.

Crude ethyl α -cyano- α -isohexate contained 28% of ethyl α -cyano- α -isomethylisohexate, b. p. 158 — $159^{\circ}/16$ mm., D_{22}^{22} 0.909, which was unaffected by long standing with cold 10% sodium hydroxide solution; the sodium hydroxide extract yielded α -cyanoisohexic acid, m. p. 47 — 48° , which was converted through the ammonium salt into the silver salt; this reacts with ethyl iodide, giving ethyl α -cyanoisohexate, b. p. $125^{\circ}/12$ mm., $241^{\circ}/749$ mm., D_{21}^{21} 0.939, which is readily hydrolysed by 10% sodium hydroxide solution.

α -Cyano- α -isohexamide, m. p. 142° , obtained by the action of concentrated ammonia solution on the ester, when heated in a vacuum with phosphorus pentachloride to 120 — 130° undergoes conversion into α -cyano- α -isohexonitrile, b. p. 121 — $122^{\circ}/18$ mm., D_{25}^{25} 0.899.
D. F. T.

Glycerol Esters of Benzoic and Myristic Acids, and the Partial Saponification of Triglycerides. ANDREAS LIPP and P. MILLER (*J. pr. Chem.*, 1913, [ii], 88, 361—394).—The author reviews

previous work on the hydrolysis of fats, and points out that, although it is now generally accepted that the hydrolysis of triglycerides takes place in stages with the intermediate formation of diglycerides and monoglycerides, only in the case of sulphuric acid as a hydrolytic agent has this view been placed beyond all doubt by the isolation of the intermediate products (compare Thieme, A., 1912, i, 333; Grün and Corelli, *ibid.*, 409). The work described in the present paper deals with the hydrolysis of tribenzoin and trimyristin by means of water and alkali hydroxides in aqueous, alcoholic and acetone solutions. It is definitely proved by the isolation of the corresponding di- and monoglycerides from the product obtained by partial saponification of the triglycerides, that in these cases also a similar hydrolysis in stages takes place.

When heated in sealed tubes at 225° in an atmosphere of carbon dioxide an equimolecular mixture of benzoic acid and glycerol yields as main product α -monobenzoin, which is freed from the accompanying $\alpha\alpha$ -dibenzoin by taking advantage of its solubility in water; the latter compound forms the chief product if the benzoic acid is in excess (2 mols.).

In agreement with the observations of Thieme (A., 1912, i, 333) on the simultaneous formation of mono- and di-glycerides by the interaction of the sodium salts of acids and glycerol α -monochlorohydrin, the authors find that the latter compound reacts at 175° with sodium benzoate, yielding a mixture of α -mono- and $\alpha\alpha$ -dibenzoin.

Glycerol $\alpha\gamma$ -dichlorohydrin and sodium benzoate at 190° give rise to α -monobenzoin, $\alpha\alpha$ -dibenzoin, and tribenzoin. $\alpha\alpha$ -Dibenzoin is an oil; the solid dibenzoin, described by Baumann (A., 1887, 229) and Grün (this vol., i, 157), probably consists of impure tribenzoin. The latter compound is obtained by shaking glycerol with benzoyl chloride (5 mols.) and aqueous sodium hydroxide at a low temperature. If less than this amount of benzoyl chloride is used, it is accompanied by varying amounts of mono- and di-benzoin (compare Baumann, *loc. cit.*, and Balbiano, A., 1903, i, 547).

The separation of mono-, di-, and tri-benzoin can be accomplished by taking advantage of the solubility of the monobenzoin in water and the greater solubility of the dibenzoin in alcohol as compared with that of the tribenzoin. When treated in alcoholic solution with 5% of the amount of potassium hydroxide, theoretically necessary for complete hydrolysis, and the mixture maintained for twenty-four hours at the ordinary temperature, tribenzoin undergoes complete decomposition into glycerol, ethyl benzoate, and potassium benzoate; if the reaction is allowed to proceed for only two minutes and the excess of potassium hydroxide at once neutralised by the addition of hydrochloric acid, then monobenzoin and dibenzoin are also formed.

The latter compounds were also isolated from the product obtained by partly hydrolysing the tribenzoin by means of potassium hydroxide in acetone at the ordinary temperature, and by heating with water in sealed tubes at 200°, both the water and potassium hydroxide being present in insufficient amount for complete hydrolysis. Partial saponification with 10% aqueous sodium hydroxide gave only di-

benzoin; the absence of the monobenzoin is referred to its solubility in water and consequent rapid hydrolysis by the sodium hydroxide.

When heated at 250° in sealed tubes in an atmosphere of carbon dioxide, a mixture of myristic acid and glycerol in equimolecular proportions yields trimyristin, *aa*-dimyristin and α -monomyristin, the latter compound forming the main product. The method adopted in separating the three compounds is based on the sparing solubility of the monomyristin in cold light petroleum, and the greater solubility in alcohol of the dimyristin in comparison with that of the trimyristin. Monomyristin (Krafft, A., 1904, i, 136) has m. p. 68°; when heated to 70° and allowed to cool slowly it solidifies at 54°; if the temperature is allowed to fall to 44° and the substance again heated, it has m. p. 55°; on further heating it solidifies at about 60° and then shows the original m. p. of 68°.

aa-Dimyristin has m. p. 64.5° (compare Grün and Theimer, A., 1907, i, 463; also *ibid.*, 464, and this vol., i, 159).

Trimyristin exists in two forms of m. p. 56.5° and 49° (compare Reimer and Will, A., 1885, 1197).

The results obtained in the partial hydrolysis of trimyristin resemble those described above in the case of tribenzoin. F. B.

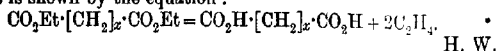
The Glycerides of Butter Fat. CONRAD AMBERGER (*Zeitsch. Nahr. Genussm.*, 1913, 26, 65—85).—Glycerides of definite composition were isolated from butter fat by subjecting the latter to fractional solution and crystallisation in ether. The most insoluble glyceride was found to consist of tristearin in the case of some butters; with other butters it was palmitylidistearin.

Stearylidipalmitin was also obtained from butter fat, proving the presence of stearic acid. W. P. S.

Tripropionin. RUDOLF W. SEUFFERT (*Zeitsch. Biol.*, 1913, 61, 551—553).—*Tripropionin* is readily obtained by the gradual addition of the calculated amount of propionic anhydride to glycerol heated at 150—165°. It has b. p. 177—182°/ca. 20 mm., n_D^{19} 1.43175. The compound is not formed by heating glycerol with propionic acid in the presence of sodium acetate, whilst, when propionyl chloride is employed under varying conditions, the product obtained invariably contains chlorine. H. W.

Catalytic Decomposition of Esters of Dibasic Organic Acids by Alumina. LOUIS MICHIELS (*Bull. Soc. chim. Belg.*, 1913, 27, 227—230).—Senderens (this vol., i, 342) has observed that ethylene, carbon dioxide, carbon monoxide, and hydrogen are formed by the decomposition of ethyl succinate in the presence of alumina at 390° and 420°, and has surmised that a diketone may also be formed under these conditions. The author has investigated this action at 260°. The main gaseous product is ethylene mixed with some carbon dioxide. The distillate consists almost entirely of succinic anhydride. Diketones or their condensation products are only present in very small quantity, since the crude distillate is almost completely soluble in alkalis.

Similarly, ethyl glutarate under the influence of alumina at 270° yields mainly ethylene and glutaric acid. In one experiment, ethyl hydrogen glutarate was also isolated. In like manner, ethyl adipate at 300—320° yields an acid distillate. The general course of the reactions is shown by the equation :

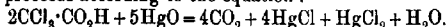


The Nitrogenous Constituent of Kephalin. A. BAUMANN (*Biochem. Zeitsch.*, 1913, 54, 30—39).—The kephalin was hydrolysed with dilute hydrochloric or sulphuric acid at 60°. From the aqueous solution, after separation of the insoluble products and the glycerophosphates (by means of lead acetate), the salt of an organic base could be separated by means of alcohol, which contains the amino-groups pre-existent in kephalin. This could be identified by means of the auri- and platin-chlorides as hydroxyethylamine. S. B. S.

Catalytic Acceleration of the Absorption of Oxygen by Lecithin with Iron Salts. TORSTEN THUNBERG (*Zeitsch. physiol. Chem.*, 1913, 87, 82); OTTO WARBURG (*Ibid.*, 83—84).—A claim for priority. Thunberg (A., 1910, ii, 323) had previously noticed that the oxidation of lecithin was accelerated by the presence of iron salts (compare Warburg and Meyerhof, this vol., i, 698). Thunberg also claims priority with reference to the influence of freezing and finely powdering the cells. Warburg denies this; he comes to precisely the opposite conclusions to Thunberg. E. F. A.

Preparation of Acetic Acid. CHEMISCHE FABRIK GRIESHEIM-ELERTON (D.R.-P. 261589).—The oxidation of acetaldehyde to acetic acid by air or oxygen proceeds satisfactorily at 70—100° or at lower temperatures (30—80°) in the presence of a catalyst, such as ferrous oxide, uranium oxide, acetic anhydride, or acetyl chloride. F. M. G. M.

Decomposition of Trichloroacetic Acid by Mercuric Oxide. KURT BRAND (*J. pr. Chem.*, 1913, [ii], 88, 342—357).—When mercuric oxide is added to a concentrated solution of trichloroacetic acid and the mixture heated to boiling, a vigorous reaction occurs, resulting in the formation of carbon monoxide, carbon dioxide, chloroform, hydrogen chloride, mercuric and mercurous chlorides; at 60° the reaction proceeds according to the equation :



The author considers that the mercuric trichloroacetate first produced decomposes into dichloromethylene, carbon dioxide, and mercuric chloride, thus : $\text{Hg}(\text{CCl}_3 \cdot \text{CO}_2)_2 = 2\text{CCl}_2 + 2\text{CO}_2 + \text{HgCl}_2$, the dichloromethylene being converted by the action of water into dihydroxymethylene, which is transformed at 60° into formic acid, and at 100° into formic acid and carbon monoxide. The formic acid is then oxidised by the mercuric chloride to carbon dioxide. The formation of chloroform during the reaction is referred to the decomposition of free trichloroacetic acid, formed from the mercuric trichloroacetate, either by hydrolysis or by the action of hydrochloric acid. F. B.

Cholic Acid. III. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1913, 87, 59—73. Compare A., 1910, i, 10; 1911, i, 10).—A re-investigation of cilianic acid and its methyl ester (compare Pregl, A., 1903, i, 318) establishes it as a tetrabasic acid, $C_{24}H_{34}O_{10}$ or $C_{24}H_{32}O_{10}$, the ester being a tetramethyl derivative. Cilianic acid is accordingly an oxidation and not a degradation product of cholic acid. The carbon dioxide formed during the oxidation is derived from the decomposition of part of the cilianic acid. E. F. A.

Seneciolic Acid. YASUHIKO ASAHINA (*Arch. Pharm.*, 1913, 251, 355—356).—Seneciolic acid, $C_8H_8O_2$, the unsaturated acid obtained from the rhizomes of *Ligularia tussilaginea* (*Senecio kaempferi*) is proved to be identical with $\beta\beta$ -dimethylacrylic acid by the direct comparison of the two acids, m. p. 69—70°, and of their calcium salts, $(C_8H_7CO_2)_2Ca \cdot 4H_2O$. C. S.

Action of Cyanides on Aldehydes and Ketones. HARTWIG FRANZEN and WALTER RYSER (*J. pr. Chem.*, 1913, [iii], 88, 293—306).—It has been shown previously (A., 1909, i, 804) that ethyl acetoacetate, ethyl benzoylacetate, and acetylacetone, when shaken with aqueous solutions of calcium, barium, strontium, and magnesium cyanides, yield crystalline salts, which were considered to be metallic derivatives of cyanohydrins, having a similar structure to that of the calcium derivative of mandelonitrile, obtained by the action of calcium cyanide on benzaldehyde.

The authors now find that the products are not nitriles, but the metallic derivatives of the ketonic esters and diketone.

The preparation of the calcium, barium, strontium, and magnesium derivatives of ethyl acetoacetate, and the calcium, strontium, and magnesium derivatives of acetylacetone is described.

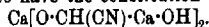
The metallic derivatives of ethyl benzoylacetate decompose very rapidly, and, therefore, could not be isolated in a pure condition.

The calcium derivative of mandelonitrile, $Ca(O \cdot CHPh \cdot CN)_2$, has been obtained in a state of purity by using an aqueous solution of calcium cyanide, prepared from calcium hydroxide and hydrocyanic acid, instead of the mixture of calcium chloride and potassium cyanide employed previously (*loc. cit.*). Its constitution has been established by its conversion into the benzoyl derivative of mandelonitrile by the action of benzoyl chloride.

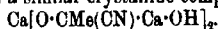
The calcium derivative of *o*-chloromandelonitrile, prepared from *o*-chlorobenzaldehyde and aqueous calcium cyanide, forms a light yellow powder.

The calcium derivatives of *p*-methylmandelonitrile and *p*-methoxy-mandelonitrile are also described.

The colourless, crystalline substance obtained by Kohn (A., 1900, i, 205) by the action of calcium cyanide on formaldehyde in aqueous solution is considered to have the constitution



Acetaldehyde yields a similar crystalline compound,



The action of potassium cyanide on acetaldehyde in aqueous solution results in the formation of alanine and α -iminodipropionic acid.

F. B.

The Action of Silicon Tetrachloride on Aldehydes and Ketones. JAMES N. CURRIE (*J. Amer. Chem. Soc.*, 1913, 35, 1961).—It has been observed that a mixture of pure acetone with silicon tetrachloride in a few hours sets to a gelatinous mass, which when broken up with water gives a brown oil consisting mainly of mesityl oxide.

Analogous results were obtained in qualitative experiments with other aldehydes and ketones.

D. F. T.

Photochemical Synthesis of Carbohydrates. JULIUS STOKLASA, JOHANN ŠEBOR, and WENZEL ZDOBNICKÝ (*Biochem. Zeitsch.*, 1913, 54, 330—332. Compare this vol., i, 18).—A further reply to the criticisms of Walther Löb (this vol., i, 250).

Behaviour of Cellulose Towards Pure Nitric Acid. II. CARL HAUSERMANN (*Zeitsch. angew. Chem.*, 1913, 26, 456. Compare *Zeitsch. angew. Chem.*, 1910, 23, 1761).—"Sulphite cellulose" is converted by cold concentrated nitric acid into nitrates without undergoing marked structural change. Treatment with nitric acid, D 1.495, 1.48, 1.47, 1.46 and 1.40, leads to the formation of nitrates containing 11.1%, 9.6%, 8.0%, 7.5%, and 2.3% of nitrogen respectively. "Sulphite cellulose" dissolves readily in warm concentrated nitric acid, and the solution, when poured into cold water, yields an amorphous product, part of which is soluble in a mixture of alcohol and ether.

Hydrocellulose prepared from cotton when treated with nitric acid, D 1.5, 1.485, 1.48, and 1.40, yields hydrocellulose nitrates containing 13.0%, 9.5%, 8.3%, and 2.3% of nitrogen respectively, whilst hydrocellulose nitrates containing 11.2%, 8.8%, 6.6%, and 2.1% of nitrogen are obtained by the action of nitric acid, D 1.495, 1.48, 1.45 and 1.40 respectively, on hydrocellulose prepared from "sulphite cellulose."

The esters derived from "sulphite cellulose" closely resemble those derived from cotton in their behaviour towards solvents, but the higher cellulose and hydrocellulose nitrates prepared from "sulphite cellulose" are not completely soluble in acetone.

W. H. G.

Benzoyl Esters of Cellulose. HERMANN OST and F. KLEIN (*Zeitsch. angew. Chem.*, 1913, 26, 437—440. Compare Hauser and Muschner, this vol., i, 363; Briggs, this vol., i, 594).—An investigation on the benzylation of cellulose, carried out primarily with the object of preparing a tribenzoate corresponding with the triacetate and trinitrate of cellulose.

Cellulose when treated with alkali hydroxide and benzoyl chloride yields a mixture of benzoates, the benzoic acid content of which is between 0 and 77%, and is dependent mainly on the proportions in which the reacting substances interact and to a slight degree on the physical state of the cellulose employed. A maximum yield of 218% of product is obtained by using a 22.4% sodium hydroxide solution in

the molecular proportions of 30 of sodium hydroxide to 1 of cellulose and 3 of benzoyl chloride to 4 of sodium hydroxide, whilst by using a 31.4% potassium hydroxide solution a maximum yield of 211% of product is obtained, the molecular proportions being the same as those just cited. The yields of product increase regularly with increase in the concentrations of the alkali up to the strengths quoted; at higher concentrations of the alkali the yields gradually decrease, and curves representing the relationship between alkali concentration and percentage of benzoic acid in the product do not show a "break" as do curves connecting alkali concentrations with the proportion of sodium combined with the cellulose (compare Vieweg, A., 1907, i, 893). A second and third treatment with alkali and benzoyl chloride increases the yield to 224% and 226% respectively, but it has not been found possible by the Schotten-Baumann method to pass beyond these values; the portion of the latter product soluble in chloroform contained 72.7% of benzoic acid, corresponding approximately with 2.5 benzoyl groups to the $C_6H_{10}O_5$ complex.

The crude benzoates may be fractionally separated by solvents; chloroform extracts 5 to 10% of a mixture containing 68 to 70% benzoic acid; aniline extracts from the portion insoluble in chloroform a mixture containing 61 to 65% of benzoic acid, whilst aniline-phenol (1:1) extracts from the residue a mixture containing 59 to 60% of benzoic acid.

Benzoates containing up to 77% of benzoic acid (a tribenzoate would contain 77.2%) are obtained by treating cellulose with benzoyl chloride in the presence of nitrobenzene and pyridine at 110–130°; the highest esters are formed when the quantity of pyridine employed is insufficient to keep the solution basic or neutral.

Solutions of cellulose benzoates in chloroform are dextrorotatory; the following values are given: tribenzoate, $[\alpha]_D$ 26–27°; ester with 70–72% of benzoic acid, $[\alpha]_D$ 20–22°.

Mercerised cellulose does not react more readily than finely divided cotton. Cellulose regenerated from "young" viscose is more reactive than that from "old" viscose; the benzoate from the former gave elastic films, whilst the benzoate from the latter gave films which were very brittle.

The yield of benzoate from hydrocellulose is less than that from cellulose, but 50% of the product containing 71–72.4% of benzoic acid is soluble in chloroform.

W. H. G.

Chemical Reactions Induced by *Bacteria aceti*. H. J. WATERMAN (*Chem. Weekblad*, 1913, 10, 718–730).—*B. aceti* isolated at low temperature rapidly transform aldoses, such as dextrose and galactose, into the corresponding monobasic acids, but has no action on ketoses. *B. aceti* isolated at high temperature does not react with either aldoses or ketoses. A summary of previous work on the action of *B. aceti* is given.

A. J. W.

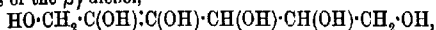
***d*-Ribose.** W. ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1913, 10, 664).—*d*-Ribose has been synthesised by converting *d*-gluconic acid into *d*-arabinose by the action of hydrogen peroxide, transformation of the pentose into *d*-arabonic acid by means

of bromine water, and conversion of this acid into *d*-ribonic acid by heating with pyridine. The ribonic acid was separated from arabinic acid by fractional crystallisation of the phenylhydrazides, and had *m. p.* 80° and $[\alpha]_D + 18.4^\circ$. On reduction with sodium amalgam, it yielded *d*-ribose, purified by conversion into its *p*-bromophenylhydrazone, *m. p.* 164°. The hydrazone was transformed into *d*-ribose by the action of benzaldehyde. It forms colourless, hygroscopic crystals, *m. p.* 95°, $[\alpha]_D - 21.5^\circ$.
A. J. W.

The Oxidation of *d*-Glucose in Alkaline Solution by Air as Well as by Hydrogen Peroxide. J. W. E. GLATTFELD (*Amer. Chem. J.*, 1913, 50, 135—157).—The author has repeated the oxidation of α -glucose by hydrogen peroxide and air in potassium hydroxide solution, and finds that in addition to glycollic acid, formic acid and carbon dioxide, isolated by Spoehr (A., 1910, i, 221) from the oxidation product, *d*-erythronic, *l*-threonic and *dl*-glyceric acids are produced.

Spoehr's α -hydroxymethyl-*d*-arabonic acid is found to be identical with *d*-arabonic acid.

The formation of the latter acid proves that glucose in the form of its $\alpha\beta$ -dienol, $\text{HO}\cdot\text{CH}:\text{C}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, dissociates into hydroxymethylene, $\text{HO}\cdot\text{CH}:$, and the methylenol of *d*-arabinose, $:\text{C}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, which is then oxidised to *d*-arabonic acid. Oxidation of the dissociation products of the $\beta\gamma$ -dienol,



gives rise to glycollic, *d*-erythronic and *l*-threonic acids, whilst the glyceric acid is formed by the dissociation and subsequent oxidation of the $\gamma\delta$ -dienol, $\text{HO}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ (compare Nef, A., 1908, i, 5).

For details of the method employed in separating the oxidation products, the original must be consulted.

The following new salts are described: *cinchonine d-arabonate*, *m. p.* 170—180°, $[\alpha]_D^{20} + 120.3^\circ$ in water, and the corresponding *strychnine* salt, *decomp.* 167—170°, $[\alpha]_D^{20} - 26.08^\circ$, *quinine* salt, *m. p.* 172—173°, $[\alpha]_D^{20} - 106.2^\circ$, and *brucine* salt, *m. p.* 167—170°, $[\alpha]_D^{20} - 26.33^\circ$.

The *strychnine* salt of *d*-erythronic acid has *m. p.* 198—199°, $[\alpha]_D^{20} - 16.84^\circ$; the *quinine* salt, *m. p.* 166°, $[\alpha]_D^{20} - 106.9^\circ$. F. B.

Biochemical Synthesis of Galactosides of Alcohols. V. β -isoButylgalactoside. ÉMILE BOURQUELOT and MARC BRIDEL (*J. pharm. chim.*, 1913, [vii], 8, 108—109).—A mixture of 95 parts of isobutyl alcohol by weight and 5 parts of water was kept for four months with galactose and emulsin. β -isoButylgalactoside was obtained in colourless needles of bitter taste, $[\alpha]_D - 11.23^\circ$.

E. F. A.

Phosphates of Magnesium and Amines. LÉONCE BARTHE (*Bull. Soc. chim.*, 1913, [iv], 13, 821—824).—The only double phosphate of magnesium and amines that has been prepared is magnesium methylamine phosphate (Barthe, A., 1905, i, 546; François, A., 1908,

i, 505). Unsuccessful attempts to prepare the corresponding salt from ethylamine are now described.

When ethylamine is added to a solution of magnesium hydrogen phosphate in dilute phosphoric acid in quantity more than sufficient for saturation, a colloidal precipitate is formed which becomes crystalline after several hours and consists entirely of magnesium phosphate. The mother liquors, when concentrated, deposit ethylamine phosphate and a further quantity of magnesium phosphate. If an excess of ethylamine is avoided, a crystalline precipitate is obtained after some hours, analysis of which shows it to be a mixture of magnesium ethylamine phosphate and magnesium phosphate or of ethylamine phosphate and magnesium phosphate. When the phosphoric acid is replaced by hydrochloric or sulphuric acids, magnesium phosphate is similarly precipitated. Analogous results are obtained by the solution of magnesium hydrogen phosphate in ethylamine hydrochloride and subsequent addition of the free amine.

Magnesium hydrogen phosphate, $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$, is most readily obtained by mixing equal volumes of 2% magnesium sulphate solution and 3% disodium hydrogen phosphate solution. A gelatinous precipitate is immediately obtained, which is rapidly transformed into a mass of fine needles.

H. W.

Preparation of the Nitrites of the Primary, Secondary, and Tertiary Amines by the Interaction of the Hydrochlorides of the Bases and Alkali Nitrites. PANCHANAN NEOGI (*Chem. News*, 1913, 108, 53—55, 62—65).—A full account of work of which an abstract has already appeared (*P.*, 1913, 29, 112).

W. G.

The Double Cadmium and Mercuric Iodides of Substituted Ammonium Bases. RASIK LAL DATTA (*J. Amer. Chem. Soc.*, 1913, 35, 949—955).—The following cadmium compounds were prepared either by adding cadmium chloride to an excess of the substituted ammonium iodide (compare *T.*, 1913, 103, 426), or by mixing solutions of cadmium iodide and the ammonium iodide in the requisite proportions. Two types of salts are obtained, namely, $2\text{NR}_4\text{I} \cdot \text{CdI}_2$ and $\text{NR}_4\text{I} \cdot \text{CdI}_2$, of which the latter is produced only in exceptional cases. The salts are white powders, sparingly soluble in water.

The double salts of cadmium iodide with tetramethylammonium, tetraethylammonium, p-tolyltrimethylammonium, pyridinium, α -picolinium, and quinolinium iodides are of the type $2\text{NH}_4\text{I} \cdot \text{CdI}_2$; tetrapropylammonium iodide gives the salt $\text{NPr}_4\text{I} \cdot \text{CdI}_2$.

When an aqueous solution of mercuric chloride is added to an excess of alkylammonium iodide, a white to yellowish-white precipitate is formed, of the type $2\text{NR}_4\text{I} \cdot \text{HgI}_2$. If the addition of mercuric chloride be continued, the precipitate changes to yellow and the salt is of the type $2\text{NR}_4\text{I} \cdot 3\text{HgI}_2$; further addition of mercuric chloride gives mercuric iodide. A solution of mercuric iodide in potassium iodide may be used instead of mercuric chloride; when the interacting solutions are strong, the type $2\text{NR}_4\text{I} \cdot \text{HgI}_2$ is produced, but this is decomposed by water and changed to the type $2\text{NR}_4\text{I} \cdot 3\text{HgI}_2$, which is the most stable of all, and is prepared by the interaction of dilute

solutions, using an excess of potassium mercuric iodide solution. The following substituted ammonium iodides give salts of both types: *tetramethylammonium*, *tetraethylammonium*, and *trimethylsulphonium* (compare Smiles, T., 1900, 77, 160) iodides. The following iodides give salts of the type $2NR_4I.HgI_2$: *tetrapropylammonium*, *p-tolyl-trimethylammonium*, *pyridinium* and *quinolinium* iodides. *p-Tolyl-trimethylammonium* iodide also gives the salt, $C_6H_4Me.NMe_3.HgI_2$.

The above salts, for the most part, vary in colour from a pale to a bright lemon yellow. They are all decomposed quantitatively into mercuric iodide on boiling with dilute nitric acid.

T. S. P.

Platini-iodides of Substituted Ammonium and Sulphonium Bases. RASIK LAL DATTA (*J. Amer. Chem. Soc.*, 1913, 35, 1185—1188).—It is found that although the platini-iodides of sodium and of the alkaline-earth metals cannot be obtained as precipitates by the interaction of chloroplatinic acid with concentrated solutions of the iodides (Datta, T., 1913, 103, 426), this method proves very convenient for the preparation of the platini-iodides of potassium, ammonium, and the amines. The method failed with hydrazine hydriodide on account of the reduction of the chloroplatinic acid to metallic platinum. In other cases the condition necessary to success is the employment of an excess of the iodide of the metal or base.

The following substances were prepared: potassium platini-iodide, very soluble, black, crystalline powder; ammonium platini-iodide, black powder; *dipropylammonium platini-iodide*, black; *tetrapropylammonium platini-iodide*, chocolate coloured; *a-picolinium platini-iodide*, black; *quinolinium platini-iodide*, jet black; *trimethylsulphonium platini-iodide*, black powder; *triethylsulphonium platini-iodide*, chocolate coloured.

D. F. T.

Non-equivalence of the Five Valencies of Nitrogen. EMIL FROMM (*Annalen*, 1913, 399, 366—370).—By reason of the great importance of the subject, Meisenheimer's recent proof (this vol., i, 595) of the non-equivalence of the five valencies of the nitrogen atom must be submitted to searching criticism before being accepted. The author is of opinion that Meisenheimer's experiments can be interpreted in another, and more probable, manner. Meisenheimer assumes that hydrogen chloride and methyl iodide both attack trimethylamine oxide at the same point and in the same manner, yielding the additive compounds $NMe_3 \begin{smallmatrix} \text{OH} \\ \text{Cl} \end{smallmatrix}$ and $NMe_3 \begin{smallmatrix} \text{OMe} \\ \text{I} \end{smallmatrix}$ respectively. From the former by the action of sodium methoxide, and from the latter by moist silver oxide, are obtained the substances $NMe_3 \begin{smallmatrix} \text{OH} \\ \text{OMe} \end{smallmatrix}$ and $NMe_3 \begin{smallmatrix} \text{OMe} \\ \text{OH} \end{smallmatrix}$; the different behaviour of the two substances during decomposition is the foundation of Meisenheimer's proof of the difference of the fifth "unique" valency of nitrogen from the other four. The author takes exception to this. The two substances $NMe_3 \begin{smallmatrix} \text{OH} \\ \text{OMe} \end{smallmatrix}$

and $\text{NMe}_3 \begin{smallmatrix} \text{OMe} \\ \text{OH} \end{smallmatrix}$, being alcoholates of a very feeble base, $\text{NMe}_3(\text{OH})_2$ must both be hydrolytically dissociated by water, and yield MeOH and $\text{NMe}_3(\text{OH})_2$ if they have the constitutions given above. He is of opinion that hydrogen chloride and methyl iodide do not attack trimethylamine oxide in the same manner. With methyl iodide the oxide forms the methiodide, $\text{NMe}_3 \cdot \text{O} \begin{smallmatrix} \text{Me} \\ \text{I} \end{smallmatrix}$; the product of the action of moist silver oxide is then $\text{NMe}_3 \cdot \text{O} \begin{smallmatrix} \text{Me} \\ \text{OH} \end{smallmatrix}$ which would be expected to yield trimethylamine, formaldehyde, and water by its decomposition, as is actually the case.

The formula $\text{NMe}_3 \cdot \text{O} \begin{smallmatrix} \text{Me} \\ \text{I} \end{smallmatrix}$ has been discussed and rejected by Meisenheimer (*loc. cit.*); the author, however, shows that the reasons for its rejection are insufficient. C. S.

Non-equivalence of the Five Valencies of Nitrogen. JAKOB MEISENHEIMER (*Annalen*, 1913, 399, 371—376).—The author replies to Fromm's criticisms (preceding abstract). In answer to his contention that two isomeric compounds should be produced by the addition of hydrogen chloride at the double linking of trimethylamine oxide if the fourth and the fifth valencies of the nitrogen atom are fundamentally different, the author claims that the whole behaviour of ammonium compounds proves that four of the valencies of the nitrogen atom are negative and the fifth is positive; therefore, in the addition of hydrogen chloride to trimethylamine oxide, the negative chlorine will become attached only to the fifth positive valency of the nitrogen atom, and only one additive compound will be produced.

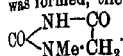
To Fromm's criticism that the two isomerides, $\text{NMe}_3 \begin{smallmatrix} \text{OH} \\ \text{OMe} \end{smallmatrix}$ and $\text{NMe}_3 \begin{smallmatrix} \text{OMe} \\ \text{OH} \end{smallmatrix}$, should both be hydrolysed by water, the author replies that only one, namely, that in which the methoxy-group is attached to the fifth positive valency of the nitrogen atom, should be hydrolytically dissociated; the other isomeride, in which the methoxy-group is bound by a negative valency, should be as little affected by water as is methoxylamine, $\text{OMe} \cdot \text{NH}_2$.

The author also criticises adversely Fromm's reasons for ascribing oxonium formulæ to substances of the types $\text{NMe}_3\text{Cl} \cdot \text{OMe}$ and $\text{NMe}_3(\text{OEt}) \cdot \text{OMe}$. C. S.

[Non-equivalence of the Five Valencies of Nitrogen.] ERIC FROMM (*Annalen*, 1913, 399, 377).—The author agrees with Meisenheimer (preceding abstract) that in ammonium compounds the fifth "positive" valency of the nitrogen atom is different from the other four "negative" valencies, but is of opinion that the results of observations on ammonium compounds cannot be applied to the case of the amino-oxides without further consideration. He claims that in amino-oxides there are two "positive" valencies which differ from the other three "negative" valencies. C. S.

Decomposition of Glucosamine by Bacteria. EMIL ABDERHALDEN and ANDOR FODOR (*Zeitsch. physiol. Chem.*, 1913, 87, 214—219).—Glucosamine hydrochloride, when decomposed by micro-organisms of the *B. subtilis* group, yields propionic acid and α -lactic acid.
E. F. A.

Fermentative Decomposition of Creatinine. DANKWART ACKERMANN (*Zeitsch. Biol.*, 1913, 62, 208—216).—Creatinine, mixed with a little dextrose and peptone, was inoculated with bacteria from a decomposing pancreas. Neither methyl- nor dimethyl-guanidine was formed, the main product of the change being 1-methylhydantoin,



E. F. A.

The Changes Produced in Asparagine by Heating its Aqueous Solutions. FELIX EHRLICH and FRITZ LANGE (*Biochem. Zeitsch.*, 1913, 54, 256—276).—By heating the ordinary asparagine with water for twelve hours and allowing the substance to crystallise out in fractions, a very small amount was obtained which has $[\alpha]_D^{20}$ 46.2°; this apparently *d*-asparagine (compare Erlennmeyer, this vol., i, 836). The authors also show that when asparagine solutions are heated, ammonia is evolved, and on crystallisation, crystals together with a non-crystallising syrup are obtained. The longer the heating takes, the smaller is the amount of crystals, the larger the amount of syrup obtainable, and the larger is the quantity of ammonia evolved. The uncrystallisable syrup is not readily freed from ammonia, and the evidence obtained indicates that it contains ammonium aspartate. The latter substance readily crystallises from water, but if its solution is heated, an uncrystallisable syrup is also obtained. It appears, therefore, to be an intermediate product produced by the action of heat on asparagine solutions. The actual nature of the final products has not yet been ascertained. S. B. S.

Resolution of *dl*-Aminohexoic Acid (Norleucine) into the Optically Active Components by means of the Formyl Compound. Polypeptides Derived from α -Aminohexoic Acid. EMIL ABDERHALDEN, C. FROELICH, and DIONYS FUCHS (*Zeitsch. physiol. Chem.*, 1913, 86, 454—468).—*dl*- α -Aminohexoic acid, which E. Fischer resolved by means of the brucine salt, is readily resolved when the brucine salts of the formyl derivatives are crystallised. The acid, for which the name norleucine is proposed, has been combined with glycine and leucylglycine to form polypeptides in the usual manner.

Formyl-dl- α -aminohexoic acid crystallises in lustrous needles, which soften at 110—111°, m. p. 114°. The optical antipodes resemble each other very closely, crystallising in slender, lustrous, short or long needles aggregated in bunches. They soften at 111°, m. p. 114°, and have $[\alpha]_D^{20}$ -15.85° and +15.53° respectively.

Chloroacetyl-d-norleucine crystallises in colourless, transparent lamellae, which soften at 70°, m. p. 104—106°, $[\alpha]_D^{20}$ +3.56°.

Glycyl-d-norleucine, $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH}_2$, forms

prisms growing into long needles, which become brown at 220°, sinter at 230°, m. p. 239—240°; they have $[\alpha]_D^{20} - 8.71^\circ$.

Glycyl-L-norleucine is almost identical in crystalline form and behaviour on heating; it has $[\alpha]_D^{20} + 8.24^\circ$.

Chloroacetyl-dl-norleucine forms long prisms, m. p. 104—107°.

Glycyl-dl-norleucine separates in fatty plates or bundles of prisms; it sinters at 210°, decomp. 215°.

α -Bromoisohexoylglycyl-dl-norleucine crystallises in platelets, m. p. 140°.

dl-Leucylglycyl-dl-norleucine separates as a crystalline skin. It sinters at 220°, decomp. 250°. It could not be hydrolysed by means of yeast juice with any certainty. The same applies to *glycyl-dl-norleucine*.

E. F. A.

Preparation of Derivatives of α -Bromoisovaleric Acid. ARTHUR LIEBRECHT (D.R.-P. 261877).— *α -Bromoisovalerylmethylamide*, needles, m. p. 103°, is obtained when *α -bromoisovaleryl bromide* is slowly dropped into a cooled 20% aqueous solution of methylamine (2 mols.); the corresponding *ethylamide*, needles, m. p. 120°, is prepared in a similar manner with ethylamine.

F. M. G. M.

Action of Hydrazine Hydrate on Dicyanodiamide and Biuret. ROBERT STOLLÉ and K. KRAUCH (*J. pr. Chem.*, 1913, [ii], 88, 306—314).—The authors have investigated the action of hydrazine hydrate on dicyanodiamide under various conditions, and find that in addition to guanazole, obtained by Hofmann and Ehrhart (A., 1912, i, 919), the following substances may be formed: aminodicyanodiamide, 1-amino-2:5-dehydrazino-1:3:4-triazole, carbonyldiazide, aminodiguanide, mono-, di- and tri-aminoguanidine.

With the exception of guanazole and the triazole, all the above-mentioned substances were isolated in the form of their benzylidene derivatives by acidifying the product of the reaction with hydrochloric acid and shaking with benzaldehyde.

The action of hydrazine hydrate on dicyanodiamide, both at 40° and at the ordinary temperature, results in the formation of guanazole, diaminoguanidine and triaminoguanidine; if the reaction is carried out at 50°, these compounds are accompanied by aminoguanidine and *aminodiguanide*, which forms a *benzylidene* derivative, m. p. 237°, $\text{NH}_2\text{C}(\text{NH}_2)\cdot\text{NH}(\text{NH})\cdot\text{NH}\cdot\text{N}:\text{CHPh}$.

Guanazole is best prepared by heating a mixture of dicyanodiamide (1 mol.) and hydrazine hydrate ($2\frac{1}{2}$ mol.) at 60—70°; if the temperature is raised to 100—110°, carbonyldiazide is formed simultaneously.

Nitrosoguanazole, $\text{C}_2\text{H}_4\text{ON}_6$, obtained as canary-yellow precipitate by the addition of sodium nitrite to a solution of guanazole in dilute acetic acid, is insoluble in the ordinary solvents, and on reduction with zinc dust and sulphuric acid yields guanazole and probably guanazine. When a large excess of hydrazine hydrate (5 mols.) is employed and the reaction carried out at 40°, dicyanodiamide yields guanazole and aminodicyanodiamidine (Thiele and Uhrfelder, A., 1899, i, 119); at the ordinary temperature, guanazole, mono-, di- and tri-aminoguanidine are formed, whilst at 70° 1-amino-2:5-dehydrazino-1:3:4-triazole

(Stollé and Bowles, A., 1908, i, 474) is the main product. Excess of hydrazine hydrate at 100—110° leads to the formation of carbohydrazide.

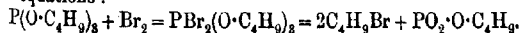
When heated with hydrazine hydrate (4 mols.) at 108—118°, biuret yields the *hydrazine* salt of hydrazidicarboxylimide [2:5-diketotetrahydro-1:3:4-triazole], $\begin{array}{c} \text{NH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CO} \end{array} > \text{NH}_2\text{N}_2\text{H}_4$, which crystallises in needles, m. p. 195°, and is converted by shaking with benzaldehyde and dilute hydrochloric acid into benzalazine and hydrazidicarboxylimide (compare Pellizzari, A., 1895, i, 73); if the reaction is carried out at 80—85°, the hydrazine salt is accompanied by aminobiuret, which was isolated in the form of its benzylidene derivative, m. p. 207° (compare Thiele and Uhrfelder, A., 1899, i, 118). F. B.

Some Hydrazine Derivatives of Chloral and Trichloroacetic Acid. ROBERT STOLLÉ and FR. HELWERTH (*J. pr. Chem.*, 1913, [ii], 88, 315—318).—Chloralhydrazine (Knöpfer, A., 1911, i, 704; this vol., i, 703) is readily obtained by the gradual addition of hydrazine hydrate to a well cooled ethereal solution of chloral hydrate. It separates from alcohol in white needles, m. p. 100° (Knöpfer gives 85°), and decomposes when kept, yielding hydrazine hydrochloride. With benzaldehyde in aqueous solution it forms the *benzylidene* derivative, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$, crystallising in small needles, m. p. 65° (decomp.).

s-Bistrichloroacetylhydrazide, m. p. 195°, $\text{N}_2\text{H}_2(\text{CO}\cdot\text{CCl}_3)_2$, prepared by heating hydrazine monohydrochloride with trichloroacetyl chloride on the water-bath (compare L. and P. Spiegel, A., 1907, i, 507), reacts with alcoholic silver nitrate and ammonia, yielding a yellow *silver* derivative, and when heated with phosphorus pentachloride or thionyl chloride is converted into 2:5-bistrichloromethyl-1:3:4-oxadiazole, $\text{CCl}_3\cdot\text{C} \begin{array}{c} \text{N}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{array} > \text{C}\cdot\text{CCl}_3$, which has m. p. 121°/9 mm., and separates from ether in long prisms, m. p. 48°. F. B.

isoButyl Ester of Phosphorous Acid. I. ALEXANDER E. ARBUZOV and A. A. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 681—690).—*Diisobutylphosphorous acid*, $\text{P}(\text{O}\cdot\text{C}_4\text{H}_9)_2\text{OH}$, obtained by Arbuzov's method for obtaining esters of this type (A., 1907, i, 8, 174, 275), is a colourless, mobile liquid with a pleasant, fruity odour, b. p. 117.5°/14 mm., 235—236°/760 mm., D_4^{20} 0.9941, D_4^{25} 0.9776, D_4^{30} 0.9940, D_4^{35} 0.9759. With metallic sodium it yields a sodium salt stable at high temperatures; the *silver* salt, $\text{P}(\text{OC}_4\text{H}_9)_2\text{OAg}$, was analysed.

isoButyl phosphite, $\text{P}(\text{O}\cdot\text{C}_4\text{H}_9)_3$, separated from its mixture with the preceding compound (A., 1907, i, 8) by converting the latter into sodium salt and distilling, is a colourless, mobile liquid with an intense peculiar odour, b. p. 100.5°/4.5 mm., 234—235°/760 mm., D_4^{20} 0.9193, D_4^{25} 0.9052, D_4^{30} 0.9193, D_4^{35} 0.9036. It reacts with bromine according to the equations:

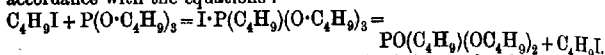


With cuprous iodide it forms the compound, $\text{CuI} \cdot \text{P}(\text{O} \cdot \text{C}_4\text{H}_9)_3$, m. p. about 48° .

It is evident that the impossibility of separating the two esters, $\text{P}(\text{O} \cdot \text{C}_4\text{H}_9)_2 \cdot \text{OH}$ and $\text{P}(\text{O} \cdot \text{C}_4\text{H}_9)_3$, by fractional distillation is due to the fact that the two liquids and mixtures of them have almost identical boiling points.

T. H. P.

Isomeric Change of $\text{P}(\text{OC}_4\text{H}_9)_3$ into $\text{C}_4\text{H}_9 \cdot \text{PO}(\text{OC}_4\text{H}_9)_2$. II. ALEXANDER E. ARBUZOV and A. A. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 690—694).—When heated with isobutyl iodide, isobutyl phosphite (see preceding abstract) undergoes isomeric change in accordance with the equations:



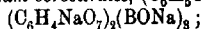
The isobutyl isobutylphosphite thus obtained is a colourless, mobile liquid, b. p. 133.5 — $134^\circ/10$ mm., 258 — $259^\circ/760$ mm., D_4^{20} 0.9630, D_4^{25} 0.9475, D_4^{30} 0.9628, D_4^{35} 0.9459. The corresponding isobutylphosphorous acid was obtained in crystals, $2\text{O} \cdot \text{P}(\text{C}_4\text{H}_9)(\text{OH})_2 \cdot \text{H}_2\text{O}$, m. p. 124° ; this acid was originally prepared by Hofmann (A., 1873, 883) as a waxy and evidently impure mass, m. p. 100° .

T. H. P.

Compounds of Boric Acid and Mannitol. FERNANDO AGENO and ELENA VALLA (*Gazzetta*, 1913, 43, ii, 163—174).—Solubility measurements indicate that the combination of boric acid and mannitol takes place in equimolecular proportions. The stability constant at 25° is 0.598; it decreases when the temperature increases. The concentration of the hydrogen ions in solutions of mannitoboric acid has been determined, the dissociation constant being of the same order of magnitude as those of the monobasic organic acids, and it is proportional to the concentration of the mannitol. The rotatory power of solutions of sodium metaborate and mannitol is proportional to the concentration of the mannitol.

R. V. S.

Preparation of Readily Soluble Stable Compounds of Perborates. VEREINIGTE FABRIKEN FÜR LABORATORIUMSBEDARF (D.R.P. 261633).—The following complex salts are prepared by mixing the required proportions of the components in aqueous solution and evaporating to dryness: sodium borotartrates, $\text{C}_6\text{H}_4\text{O}_6(\text{BONa})$ or $\text{C}_6\text{H}_5\text{NaO}_6(\text{BONa})$; sodium borocitrates, $(\text{C}_6\text{H}_5\text{O}_7)_2(\text{BONa})_3$ or



aluminium sodium tartrates, $\text{NaOAl}(\text{C}_4\text{H}_4\text{O}_6)_2\text{Na}_3$ or $\text{Al}(\text{C}_4\text{H}_4\text{O}_6)_3\text{Na}_3$. When moist they are of a syrupy consistency, but can be dried to masses resembling water glass and then reduced to powder.

F. M. G. M.

Preparation of Chlorobenzenedisulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.P. 260563).—When *p*-chlorobenzenedisulphonyl chloride is heated with fuming sulphuric acid (4 parts) at 160 — 180° with continual stirring, it furnishes a chlorobenzenedisulphonic acid (compare A., 1892, 331).

F. M. G. M.

Preparation of meso-Halogenanthracene- β -sulphonic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 260562).—*Dichloroanthracenesulphonic acid*, a yellow powder, somewhat soluble in and exhibiting a blue fluorescence in water, is obtained when dichloroanthracene (1 part) in chloroform (100 parts) at 30° is treated with chlorosulphonic acid and the temperature subsequently maintained at 40° for four hours; the reaction can also be carried out in fuming sulphuric acid.

Dibromoanthracenesulphonic acid is obtained in a similar manner from dibromoanthracene. F. M. G. M.

Preparation of Iodo-derivatives of *p*-Hydroxy- β -phenylethylamine and of its *N*-Alkyl Derivatives. F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 259193).—The iodo-derivatives of *p*-hydroxy- β -phenylethylamine have an enhanced therapeutic value. *Di-iodo-p-hydroxy- β -phenylethylamine*, glistening, colourless needles, m. p. 189–190°, is obtained when an aqueous solution of *p*-hydroxy- β -phenylethylamine is slowly treated with iodine and sodium hydroxide; any great excess of alkali is to be avoided during the reaction; the *hydriodide* separates in yellowish-brown leaflets, and is decomposed with sodium carbonate in the usual manner.

N-Benzyl-p-hydroxy- β -phenylethylamine hydrochloride, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\text{Ph}\cdot\text{HCl}$, needles, m. p. 216°, is prepared from benzaldehyde and *p*-hydroxy- β -phenylethylamine with subsequent reduction (with sodium amalgam) of the Schiff base, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}\cdot\text{CHPh}$; when treated with iodine, it furnishes *N-benzyl-di-iodo-p-hydroxy- β -phenylethylamine*, yellow needles, m. p. 159–160° (decomp.).

Piperonyl-p-hydroxyphenylethylamine, m. p. 115° (the *hydrochloride* has m. p. 219°), on similar treatment gives rise to a *N-piperonyldi-iodo-p-hydroxyphenylethylamine*, decomp. m. p. 165°. F. M. G. M.

Preparation of *N*-Alkylaryl Derivatives of *p*-Hydroxy- β -phenylethylamines. F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 259874).—The Schiff base obtained from benzaldehyde and *p*-hydroxy- β -phenylethylamine (compare preceding abstract) has m. p. 148°; *N-benzyl-p-hydroxy- β -phenylethylamine* forms colourless needles, m. p. 143°; whilst the Schiff base (*loc. cit.*) prepared from piperonaldehyde and *p*-hydroxy- β -phenylethylamine has m. p. 151°.

When *p*-hydroxy- β -phenylethylamine is combined with veratraldehyde it furnishes a Schiff base, m. p. 114°, which on reduction gives rise to *N-veratryl-p-hydroxy- β -phenylethylamine*, m. p. 118°; the *hydrochloride* has m. p. 215°, whilst with salicylaldehyde it yields a Schiff base, yellow needles, m. p. 145°, and on reduction *N-o-hydroxybenzyl-p-hydroxy- β -phenylethylamine*, colourless needles, m. p. 115°.

F. M. G. M.

The Condensation of Vanillin and Piperonal with Certain Aromatic Amines. ALVIN S. WHEELER (*J. Amer. Chem. Soc.*, 1913, 35, 976–978. Compare A., 1909, i, 673; 1908, i, 332; 1903, i, 246).—An extension of the earlier investigations. In boiling toluene

solution, vanillin slowly condenses with *p*-aminobenzoic acid with formation of 4-hydroxy-3-methoxybenzylidene-*p*-aminobenzoic acid, deep yellow plates, m. p. 211—212°, which on recrystallisation from water separates as a brilliant red substance with one molecule of water; on expelling the water at 100° the original yellow colour is restored.

Vanillin condenses with ethyl *p*-aminobenzoate in boiling benzene solution, giving ethyl 3-methoxy-4-hydroxybenzylidene-*p*-aminobenzoate, thin, yellow plates, m. p. 145° (corr.).

Under similar conditions to the last, vanillin and *p*-anisidine produce 4-hydroxy-3-methoxybenzylidene-*p*-anisidine, pale yellow crystals forming radiating clusters, m. p. 133.5° (corr.); with piperonal and *p*-anisidine, 3:4-methylenedioxybenzylidene-*p*-anisidine, very pale yellow needles, m. p. 117.5° (corr.), is obtained.

Piperonal and *p*-aminobenzoic acid condense slowly in boiling toluene solution, yielding 3:4-methylenedioxybenzylidene-*p*-aminobenzoic acid, pale yellow prisms, 233—234°. If the heating is less prolonged, or if an excess of the acid is taken, a substance, m. p. 171—174°, is obtained in considerable quantity.

When heated together in boiling benzene solution, piperonal and ethyl *p*-aminobenzoate undergo condensation to ethyl 3:4-methylenedioxybenzylidene-*p*-aminobenzoate, long, pale yellow needles, m. p. 169° (corr.).

D. F. T.

Preparation of Benzoylchloroamide. RASIK LAL DATTA and TARAPADA GHOSH (*J. Amer. Chem. Soc.*, 1913, 35, 1044—1045).—Benzoylchloroamide is conveniently prepared by passing chlorine into an aqueous suspension of powdered benzamide until a sample of the solid, after separation and recrystallisation, has m. p. 116°; the process usually occupies several hours.

If the method used by Bender (*Ber.*, 1882, 15, 410) for the preparation of this substance is modified by adding acetic acid and then a concentrated solution of bleaching powder to an aqueous suspension of benzamide, the product is a substance, m. p. 153—163°.

D. F. T.

Molecular Rearrangements of Carbon Compounds. II. Aromatic (N)-Acylamines and the Beckmann Rearrangement. CLARENCE G. DERICK and J. H. BORNHANN (*J. Amer. Chem. Soc.*, 1913, 35, 1269—1289. Compare Derick, A., 1910, i, 805).—Further experimental evidence is produced in favour of the decision in the earlier investigation that non-reversible intramolecular rearrangements of carbon compounds take place in the direction to decrease the ionisation constant. For the purpose of determination of the small ionisation constants of acylamines, a colorimetric method based on the colours produced with suitable indicators has been developed, by means of which the ionisation constant of sufficiently soluble acids and bases may be estimated with a mean error of 2%.

In accord with the view expressed above it is found that each of such substances as acetanilide, propionanilide, benzanilide, and chloroacetanilide, which do not rearrange to monoacylaminoketones, has a

lower ionisation constant (basic) than the corresponding isomeride of the latter type. On the other hand, the aromatic diacylamides, for example, diacetanilide and dipropionanilide, which can undergo rearrangement (Chattaway, T., 1904, 386, 1181, etc.), are found to have higher ionisation constants (acidic) than their isomerides, *p*-acetylaminooacetophenone and *p*-propionylaminopropiophenone, which ionise as bases.

The results generally indicate that acyl radicles derived from acids with ionisation constants between 1.4×10^{-5} and 1.55×10^{-3} at 25° must be twice substituted at the nitrogen atom of aniline before isomeric change will be possible.

In the case of the Beckmann rearrangement, which has been studied with acetophenoneoxime and benzophenoneoxime, it is again found that the ionisation constants (basic) of these substances are greater than those of acetanilide and benzanilide, into which they pass by isomeric change.

p-Propionylaminopropiophenone, long, colourless needles, m. p. 151° (corr.), was obtained by the action of propionyl chloride on *p*-aminopropiophenone, and also by warming propionylanilide with propionyl chloride and aluminium chloride in carbon disulphide. The method adopted by Čech (A., 1878, 51) proved unsatisfactory for the preparation of chloroacetanilide, and it was found that much better results were obtainable by allowing aniline and chloroacetic acid to react in cooled ethereal solution and keeping the resulting aniline chloroacetate with the calculated quantity of phosphoric oxide in a well stoppered bottle for several weeks.

D. F. T.

A New Method of Synthesising the Higher Phenols. TREAT B. JOHNSON and WILLARD W. HODGE (*J. Amer. Chem. Soc.*, 1913, 35, 1014—1023).—It is found that mixed ketones containing hydroxyl or alkyloxy radicles in the benzene nucleus are readily and smoothly reducible by zinc amalgam and hydrochloric acid to form the corresponding alkyl-substituted phenols or ethers. The reaction appears to be a general one. Only those products which are described for the first time are mentioned below.

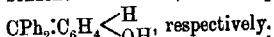
1-Acetyl-2:4-dihydroxybenzene is reduced by the above agent to 2:4-dihydroxy-1-ethylbenzene, prismatic crystals, m. p. $98-99^\circ$. The corresponding propionyl compound gives 2:4-dihydroxy-1-propylbenzene prisms, m. p. $82-83^\circ$.

2-Propionyl-1:4-dihydroxybenzene becomes converted into 1:4-dihydroxy-2-propylbenzene, microscopic needles, m. p. 86° . 2-Propionyl-1:4-dimethoxybenzene, a pale yellow oil, b. p. $167-169^\circ/13$ mm., obtained by the action of propionyl chloride and aluminium chloride on a solution of quinol dimethyl ether in light petroleum, on reduction yields 1:4-dimethoxy-2-propylbenzene (Thoms, A., 1903, i, 415).

It is noteworthy that whereas the reduction of 1-chloroacetyl-3:4-dihydroxybenzene by this new method proceeds satisfactorily giving a good yield of 3:4-dihydroxy-1-ethylbenzene, the action of zinc and hydrochloric acid, as has already been shown (Dziergowski, A., 1894, i, 73), leads only to the formation of 1-acetyl-3:4-dihydroxybenzene.

D. F. T.

Triphenylmethyl. XXIII. Tautomerism of the Hydroxytriphenylcarbinols. MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1913, 35, 1035—1042).—The conflicting results as to the properties of *p*-hydroxytriphenylcarbinol (Bistrzycki and Herbst, A., 1903, i, 639; 1904, i, 44; Baeyer and Villiger, A., 1903, i, 813; Auwers and Schröter, A.; 1903, i, 820) are readily explicable when it is borne in mind that tautomerism has been observed with such related compounds as triphenylmethyl and the triarylcarynyl haloids (A., 1909, i, 144). There exist two forms of hydroxytriphenylcarbinol, probably of the benzenoid structure, $\text{OH}\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, and the quinonoid structure, $\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, respectively:



The hydroxycarbinol is best prepared by demethylating *p*-anisyl-diphenylcarbinol with aluminium chloride in benzene. The product is digested with 3% sodium hydroxide solution, when, after filtration, the addition of excess of acetic acid precipitates the yellow quinonoid modification; this, after recrystallisation from 40—50% acetic acid, has m. p. 139—140°, whilst separation of the carbinol from the alkaline solution by addition of ammonium chloride solution gives the colourless benzenoid form, which, after crystallisation from aqueous alcohol containing a little ammonia, forms needles or plates, m. p. 157—159°, or sometimes 162—163° (compare Auwers and Schröter, *loc. cit.*).

The two forms are not physical isomerides, for a solution of each crystallises only in the original form even when inoculated with a crystal of the other. On heating the solids, the quinonoid modification commences to undergo dehydration below 60°, whilst the benzenoid modification begins to turn yellow in the neighbourhood of 100°, probably due to isomerisation, and simultaneously commences to lose water.

The yellow modification is always obtained when either form is crystallised from acetic acid, whilst the colourless modification is invariably the result if an alkaline solution is treated with ammonium chloride or if crystallisation is effected from alcohol containing some ammonia. Recrystallisation of either form from alcohol containing hydrochloric acid usually gives a mixture of yellow and colourless crystals, whilst alcohol alone induces tautomerisation but slowly.

Exposure to sunlight or ultraviolet radiation causes a fairly rapid and complete change of the colourless benzenoid to the yellow quinonoid tautomeride, so that, from analogy to the stereoisomeric ethylenic compounds, the latter is presumably the labile modification.

Hydrogen chloride is absorbed by both isomerides in the solid state with formation of the same chloride, $\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{HCl}$, a deep red, iridescent solid apparently identical with the product of the action of hydrogen chloride on fuchson; when treated with molecular silver this *p*-hydroxytriphenylcarbinyl chloride loses hydrogen chloride and gives rise to fuchson.

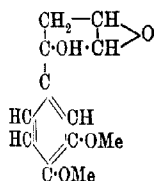
It is found that this behaviour is apparently general for the *p*-hydroxytriphenylcarbinols, and that, also, *o*-cresyldiphenylcarbinol (compare Bistrzycki and Zurbriggen, A., 1904, i, 44) gives two modifications which can be best isolated by the methods applied above.

there exists similar relations between the modifications of high and low m. p., as regards colour and behaviour towards light. D. F. T.

Identification of "Jambulol" as Ellagic Acid. FREDERICK B. POWER and THOMAS CALLAN (*Pharm. J.*, 1913, 91, 245).—Further examination of the substance present in jambul seeds, to which the name "jambulol" was given previously by the authors (A., 1912, ii, 480) shows that it is identical with ellagic acid (compare T., 1905, 87, 1412). W. P. S.

The Crystalline Deposit Occurring in the Timber of the "Colonial Beech" [*Gmelina Leichhardtii*, F.v.M.]. HENRY G. SMITH (*J. Roy. Sci. New South Wales*, 1913, 46, 187—200).—The author has examined the white deposit which frequently fills the cells of the wood and accumulates in the cracks of *Gmelina Leichhardtii*; he proposes to name this, *gmelinol*. It separates from hot water in needle prisms or plates. In the crystalline state it has m. p. 122° (corr.) and, after cooling, solidifies to a transparent, resin-like substance, m. p. 62—63°. The latter m. p. remains unchanged after many weeks if the material is preserved in the glassy condition in the lump, but, if the fused substance is powdered, the m. p. immediately commences to rise, and, after a comparatively short time, has reached about 120—121°, but does not appear to revert quite to the m. p. of the original crystals. It has $[\alpha]_D +123.8^\circ$ when dissolved in chloroform. It dissolves in 1470 parts of water at 22°. Analyses and determination of molecular weight indicate the formula $C_{13}H_{14}O_4$. Nitric acid converts it into a dinitro-compound, $C_{13}H_{12}O_4(NO_2)_2$, m. p. 128—129°. Sodium acetate and acetic anhydride transform it into a *monoacetyl* derivative, m. p. 110°.

When an excess of bromine water is added to an aqueous solution of the substance, a light drab substance, $C_{13}H_{11}O_4Br$, is formed, which is not distinctly crystalline, and melts at about 100°, after much darkening at about 90°. The bromine atom must have been introduced into the side-chain, since it can be eliminated by boiling with alcoholic silver nitrate solution. Zeisel determinations indicate the presence of two methoxy-groups, and this is confirmed by the production of veratric acid when the substance is oxidised by a



solution of chromic acid in glacial acetic acid, or by alkaline permanganate. When fused with potassium hydroxide at a temperature not exceeding 200°, phenolic substances are formed, whilst, at 210—225°, protocatechuic acid is produced, together with small quantities of a volatile acid.

From the above experiments, and from the red and green colorations given by the vapour of the substance to pine wood moistened with hydrochloric acid, the author is led to propose tentatively the annexed formula for *gmelinol*.

H. W.

Preparation of *N*-Monoalkyl Derivatives of *p*-Aminophenols. EMMANUEL MERCK (D.R.-P. 260234. Compare A., 1909, i, 222).—*N*-Alkyl derivatives of *p*-aminophenols are readily prepared by the

action of primary aliphatic amines on the alkali derivatives of quinol at a temperature of 200—250° for five to twenty hours, either in the presence or absence of condensing agents; this reaction, moreover, can be carried out in aqueous solution or in the absence of a solvent.

Details are given of several modifications of these methods for preparing *N*-methyl-*p*-aminophenol from methylamine and quinol in the presence of sodium ethoxide, or of sodium carbonate either with or without the addition of zinc chloride or other condensing agents.

F. M. G. M.

Derivatives of Phenacyl Sulphide and their Stereoisomerism. EMIL FROMM and WILHELM SCHÖMER (*Annalen*, 1913, 399, 353—365).—*Dibenzylidenediphenacyl sulphide*, $S(CBz:CHPh)_2$, m. p. 270°, leaflets, is obtained from phenacyl sulphide, benzaldehyde, and sodium hydroxide in 50% alcohol. Diphenacyl sulphide and bromine in chloroform at 0° yield at first a yellow precipitate of the unstable *diphenacyl sulphide dibromide*, but ultimately *dibromodiphenacyl sulphide*, $C_{16}H_{12}O_2SBr_2$, m. p. 107°, white crystals, is obtained. The *di-iodide*, $I_2S(CH_2:COPh)_2$, m. p. 121°, red needles, is more stable, and is prepared in a similar manner.

Equal molecular quantities of diphenacylsulphoxide and phenylhydrazine in neutral or in acid solution yield *diphenacylsulphoxidophenylhydrazine*, $C_{22}H_{20}O_2N_2S$, m. p. 186°. Diphenacylsulphoxide and hydroxylamine hydrochloride, with or without sodium carbonate, yield *diphenacylsulphoxidodioxime*, $C_{16}H_{16}O_2N_2S$, m. p. 206°; no other oxime or dioxime has been obtained.

Dimethyldiphenacylsulphone has the symmetrical formula,
 $SO_2(CHMe:COPh)_2$

since it is decomposed by boiling dilute sodium hydroxide into benzoic acid and diethylsulphone. Unlike diphenacylsulphone itself, dimethyldiphenacylsulphone does not condense with phenylhydrazine, semicarbazide, or hydroxylamine in acid, neutral, or alkaline solution. This inactivity apparently must be due to steric hindrance; it is not to be attributed to the existence of the sulphone in the form $SO_2(CMe:OPh:OH)_2$, because the substance does not react with acetic anhydride, benzoyl chloride, or sodium and chlorodinitrobenzene.

Diphenacylsulphone and aqueous bromine in daylight yield *dibromodiphenacylsulphone*, $C_{16}H_{12}O_4Br_2S$, m. p. 186°, prisms, after eight days, and *tetrabromodimethylsulphone*, $SO_2(CHBr)_2$, m. p. 151°, and benzoic acid after three months. Dibromodiphenacylsulphone forms a *dioxime*, $C_{16}H_{14}O_4N_2Br_2S$, m. p. 184°, needles, by boiling with hydroxylamine hydrochloride (two equivalents) and sodium carbonate, and an *oxime*, $C_{16}H_{14}O_4NBr_2S$, m. p. 158°, white needles, by boiling with alcohol and hydroxylamine hydrochloride; isomeric oximes cannot be isolated.

The behaviour of the oximes and the dioximes of diphenacylsulphone has been partly described by Fromm and Flaschen. The dioxime, m. p. 204°, has the *syn*-configuration (see below). It yields only an acetyl derivative with acetic anhydride, but by treatment with benzoyl chloride and sodium hydroxide is converted into a *dibenzoyl* derivative, $C_{20}H_{12}O_6N_2S$, m. p. 150°. The *anti*-dioxime has m. p. 209°, not 190°, as stated previously; it forms a *diacetyl* derivative, $C_{20}H_{10}O_6N_2S$.

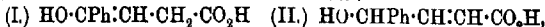
m. p. 152° , and a *dibenzoyl* derivative, $C_{20}H_{14}O_8N_2S$, m. p. 168° . Its *anti*-configuration is proved by the behaviour of the dioxime with phosphorus pentachloride in boiling ether, whereby, after treatment with water, a substance, $C_{16}H_{10}O_4N_2S$, m. p. 215° , is obtained, which must be *sulphonediaceetanilide*, $SO_2(CH_2 \cdot CO \cdot NHPh)_2$, since it is decomposed into aniline and sulphuric and acetic acids by aqueous sodium hydroxide. Consequently the dioxime, m. p. 204° , must have the *syn*-configuration, since the dioxime-anhydride, m. p. 167° , being formed from each of the phenacylsulphoneoximes, must have the *amphi*-configuration.

The configurations of the diphenacylsulphoneoximes follow from the preceding. The *syn*-dioxime can only result from the *syn*-oxime; the latter, therefore, must be the oxime, m. p. 144° , since this yields the *syn*-dioxime by treatment with hydroxylamine hydrochloride and calcium carbonate. The oxime, m. p. 173° , must therefore have the *anti*-configuration.

syn-Diphenacylsulphonedi oxime is unchanged by rapid treatment with phosphorus pentachloride and ether. When the mixture is kept for many days, it yields, after treatment with water, a substance, $C_{16}H_{10}O_4N_2Cl_2S$, m. p. 174° , yellow crystals, which is probably trichlorodiphenacylsulphonedi oxime or its transformation product, trichlorosulphonediaceetanilide; the substance, which can also be obtained from the *anti*-dioxime, is receiving further examination. C. S.

Preparation of Condensation Products from Phenol-sulphonic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 260379).—An account of the preparation of compounds, colourless powders, soluble in water, which are obtained by heating a mixture of *o*- and *p*-phenolsulphonic acids during twenty-four to seventy-two hours at 130 – 140° under 20 mm. with condensing agents, such as phosphorus trichloride or thionyl chloride. F. M. G. M.

α -Hydroxy- γ -phenylcrotonic Acid. J. BOUGAULT (*Compt. rend.*, 1913, 157, 377–379).—The author puts forward an alternative constitution for the γ -hydroxyphenylcrotonic acid obtained from the α -hydroxy-acid by boiling in aqueous solution with oxalic acid (compare this vol., i, 727). From the behaviour of the new isomeride he is unable to decide between the two formulæ:



but is now inclined to support formula II, by reason of the behaviour of the acid on oxidation with potassium permanganate. Further, he notes that the original transformation is reversible. W. G.

Isomerisation of the α -Hydroxy- β -unsaturated Acids to γ -Ketonic Acids. J. BOUGAULT (*Compt. rend.*, 1913, 157, 403–405. Compare Thiele, A., 1902, i, 152; Erlenmeyer, A., 1904, i, 1015).—The author considers that the transformation of α -hydroxyphenylcrotonic acid into *p*-benzoylpropionic acid takes place in two stages, namely: $CHPh \cdot CH \cdot CH(OH) \cdot CO_2H \rightarrow HO \cdot CHPh \cdot CH \cdot CH \cdot CO_2H \rightarrow COPh \cdot CH_2 \cdot CH_2 \cdot CO_2H$.

The first stage has already been shown to take place under the

influence of dilute acids (compare preceding abstract), and since the second step can be brought about equally well by acids and alkalis, the intermediate formation of lactones (compare Thiele and Erlenmeyer, *loc. cit.*) is not necessary. W. G.

Action of Light on Esters of α -Cyanocinnamylideneacetic Acid. II. MARIE REIMER and ELEANOR KELLER (*Amer. Chem. J.*, 1913, 50, 157—171).—In continuation of previous work (A., 1911, i, 447), the authors have examined the behaviour of the methyl, ethyl, propyl, isopropyl, and isobutyl esters of α -cyanocinnamylideneacetic acid on exposure to light, both in the solid condition and also in solution. Without solvent all the esters polymerise to a dimeric form, the reaction being practically quantitative, except in the case of the stable ethyl ester, which is considerably oxidised. In alcoholic solution only the methyl ester undergoes polymerisation; the ethyl ester is transformed into an unstable isomeride, whilst the remaining esters undergo slight oxidation. Similar results were obtained in benzene solution. The behaviour of the isomeric ethyl and isobutyl esters has also been studied. On exposure to light without solvent, the isomeric ethyl esters polymerise to dimeric forms, which are not identical but structurally isomeric (compare *loc. cit.*); at the same time the stable form is partly oxidised, whilst the unstable form is not.

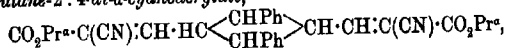
In benzene and alcoholic solution the stable ethyl ester is transformed into the unstable isomeride; the reverse reaction does not take place. The isomeric isobutyl esters behave in a similar manner.

From these results the conclusion is drawn that the action of light on ethylenic compounds is determined, not only by the nature of the groups, but also by the spatial configuration of the molecule.

The anomalous behaviour of the cinnamylidene compounds described by Stobbe (this vol., i, 177) may be explained on the assumption that in this series, compounds of different configuration were compared.

The unstable ethyl α -cyanocinnamylideneacetate crystallises in flat, straw-coloured needles, m. p. 113°.

Propyl α -cyanocinnamylideneacetate, prepared by the condensation of cinnamaldehyde with propyl cyanoacetate by means of potassium propyloxide in propyl-alcoholic solution, forms long, flat, orange crystals, m. p. 107°, and is converted by light into *propyl 1:3-diphenylcyclobutane-2:4-di- α -cyanoacrylate*,



which crystallises in white needles, m. p. 107—108°, and is oxidised by potassium permanganate in acetone solution to α -truxillic, benzoic and oxalic acids.

isoPropyl α -cyanocinnamylideneacetate, prepared in a similar manner, forms lemon-yellow plates, m. p. 111—112°, and on exposure to light yields *isopropyl 1:3-diphenylcyclobutane-2:4-di- α -cyanoacrylate*, crystallising in needles, m. p. 136°. The stable form of *isobutyl α -cyanocinnamylideneacetate*, prepared by esterifying the acid by the hydrogen chloride method, forms yellow plates, m. p. 114°, and is converted by light into *isobutyl 1:3-diphenylcyclobutane-2:4-di- α -cyanoacrylate*, crystallising in glistening, white needles, m. p. 123°.

The unstable *isobutyl* ester is prepared by the condensation of cinnamaldehyde with *isobutyl* cyanoacetate. It forms yellow plates, m. p. 110—111°, and by boiling with an *isobutyl*-alcoholic solution of hydrogen chloride is transformed into the stable form. On exposure to light, it polymerises to a dimeric form, $C_{33}H_{34}O_4N_2$, m. p. 114—115°, the constitution of which has not yet been established. F. B.

Phototropy. II. FERDINANDO GRAZIANI and F. BOVINI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 32—41. Compare this vol., i, 984).—The hydrazones described in the present paper of the type



are not phototropic, resembling in this respect those of the type $R'R''N:N:CHR$ previously investigated. The phenomenon is therefore associated only with hydrazones of the type $R'NH:N:CHR$, and these must not contain a substituent in the ortho-position of the nucleus of the group R' . The explanation of the phototropy of the hydrazones would then be the mobility of the hydrazinic hydrogen atom, which is displaced to the ortho-position of the nucleus of the group R' by waves of short length, whilst those of great length, including those of heat, reproduces the original, stable form of the hydrazone. Of the hydrazones mentioned in this paper, the following have not previously been prepared:

Cuminaldehydephenylmethylhydrazone, $MePhN:N:CH \cdot C_6H_4 \cdot CHMe_2$, forms pale yellow needles, m. p. 54°.

Cinnamaldehydephenylmethylhydrazone, $MePhN:N:CH:CH:CHPh$, crystallises in intensely yellow needles, m. p. 114°.

Salicylaldehydephenylmethylhydrazone has m. p. 74° (Labhardt and V. Zembruski, A., 1900, i, 125, gave 71°).

Piperonaldehydephenylmethylhydrazone has m. p. 88° (Goldschmidt, A., 1897, i, 54, gave 85°).

p-Tolualdehydephenylmethylhydrazone, $MePhN:N:CH \cdot C_6H_4Me$, crystallises in soapy, yellowish-green leaflets, m. p. 122°.

Vanillinphenylmethylhydrazone, $MePhN:N:CH \cdot C_6H_4(OH) \cdot OMe$, forms colourless needles, m. p. 122°.

Cinnamaldehydephenylbenzylhydrazone,
 $CH_2Ph \cdot NPh:N:CH:CH:CHPh$,

is a lemon-yellow, crystalline powder, m. p. 167—168°.

Piperonalphenylbenzylhydrazone, $CH_2Ph \cdot NPh:N:CH \cdot C_6H_3O_2 \cdot CH_2$, forms pale yellow needles, m. p. 124°.

p-Tolualdehydephenylbenzylhydrazone, $CH_2Ph \cdot NPh:N:CH \cdot C_6H_4Me$, crystallises in colourless, silky needles, m. p. 123—124°.

Phenyl-β-naphthylhydrazine may be prepared by reducing the corresponding nitrosoamine with zinc and acetic acid.

Benzaldehydephenyl-β-naphthylhydrazone, $C_{10}H_7 \cdot NPh:N:CHPh$, forms yellow needles, m. p. 92—93°.

Anisaldehydephenyl-β-naphthylhydrazone,
 $C_{10}H_7 \cdot NPh:N:CH \cdot C_6H_4 \cdot OMe$,
 crystallises in almost colourless, prismatic needles, m. p. 116—117°.

Cuminaldehydephenyl-β-naphthylhydrazone,
 $C_{10}H_7 \cdot NPh:N:CH \cdot C_6H_4 \cdot CHMe_2$,
 forms colourless needles, m. p. 118°.

Cinnamaldehydephenyl-β-naphthylhydrazones,
 $C_{10}H_7 \cdot NPh \cdot N \cdot CH \cdot CH \cdot CHPh$,

forms pale yellow, acicular crystals, m. p. 156°.

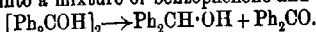
p-Tolualdehydephenyl-β-naphthylhydrazones forms yellow, acicular crystals, m. p. 154°.

R. V. S.

Reduction of Aromatic Ketones. JACOB BÖRSEKEN and W. D. COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 91—99).—The authors have made an approximate quantitative study of the reduction of benzophenone by zinc dust and aluminium amalgam in neutral, faintly acid, faintly alkaline, and strongly alkaline alcoholic solutions. For this purpose, quantities of 5 grams of benzophenone were boiled under reflux for definite intervals, with the requisite amount of reducing agent in 50 c.c. of 80% alcohol, filtered hot, made up to 100 c.c., and shaken at 25° for a day. Benzopinacone, being practically insoluble, was then filtered off, if produced at all, and some of the filtrate was evaporated and the residue weighed and examined.

In a neutral solution, zinc dust had no action, but aluminium amalgam produced 32% of pinacone and 68% of pure benzhydrol. In a very faintly acid solution, in a current of carbon dioxide or in presence of ammonium chloride, zinc dust gave rise exclusively to the pinacone. In acetic acid solution both metals produced the pinacone, together with some pinacolone and diphenylmethane, but no benzhydrol. In presence of free ammonia the product was almost exclusively the hydrol, although a small amount of the pinacone was obtained. In a strongly alkaline solution the sole product with zinc dust was benzhydrol (compare Montagne, A., 1907, i, 14), whilst aluminium and magnesium amalgams and sodium gave, in addition, traces of diphenylmethane.

The chief controlling factor is therefore the reaction of the medium. As long as it is acid the pinacone is the sole product, but as soon as hydroxyl ions are present the hydrol appears. In the case of aluminium amalgam in aqueous alcohol it is assumed that a slight excess of these ions occurs at the surface of the metal. As the excess of hydroxyl ions increases, the pinacone can no longer exist, since it is easily converted into a mixture of benzophenone and benzhydrol,

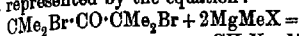


The first product of the reduction is assumed to be, in all cases, the half-pinacone, Ph_2COH ; this would polymerise at once to the pinacone, which would remain unchanged, unless the concentration of hydroxyl ions were such that it would be resolved into the hydrol and the ketone with appreciable velocity. In alkaline solution the half-pinacone might also be reduced directly to the hydrol, but the above assumption would account for the occurrence of a little pinacone in solutions with very low hydroxyl-ion concentration.

The latter point was verified by the reduction of several substituted benzophenones by means of aluminium amalgam in 80% alcohol. The methoxy- and methyl groups appear to favour the formation of pinacone, but halogens in the nucleus, and especially a number of them, have the opposite effect; thus *pp'*-dichlorobenzophenone gave 96% of hydrol and 4% of pinacone. In dilute acetic acid solution with zinc

dust, however, it gave a quantitative yield of *tetrachlorobenzopinacone*, $C_{10}H_{18}O_2Cl_4$, m. p. 180° .
J. C. W.

Action of Magnesium Phenyl Bromide on Di- α -bromoisopropyl Ketone. (Mlle.) ANNA I. UMNova (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 881—884).—From a study of the products obtained by the interaction of magnesium methyl bromide (or iodide) and di- α -bromoisopropyl ketone (this vol., i, 7), it is supposed that the reaction is represented by the equation:



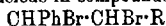
$CH_3X + MgBrX + CMe_2 \cdot CO \cdot CMe_2 \cdot MgBr$,
the action of water then yielding isopropyl *tert*-butyl ketone. This supposition is supported by the liberation of a gas burning with a green flame when methyl bromide is employed, and by the formation of silver iodide when the ethereal extract of the products obtained with methyl iodide is treated with silver nitrate; the formation of methyl iodide was not, however, directly proved.

If, however, magnesium phenyl bromide is used in the reaction in place of the magnesium methyl compound, bromobenzene is found to be liberated. In one case, the complex magnesium ketonic compound was treated with water so as to yield α -phenylisopropyl isopropyl ketone, and in another with carbon dioxide to give the corresponding β -ketonic acid.

a-Phenylisopropyl isopropyl ketone, $CPhMe_2 \cdot CO \cdot CHMe_2$, b. p. $118-119^\circ/12$ mm., $243-244^\circ/760$ mm., could not be obtained quite free from diphenyl. Its bromo-derivative, $C_{15}H_{17}OBr$, forms stout prisms, m. p. $64-65^\circ$, apparently containing alcohol of crystallisation, and has the normal molecular weight in freezing benzene.

The ketonic acid, $CPhMe_2 \cdot CO \cdot CMe_2 \cdot CO_2H$, m. p. $90-91^\circ$ (decomp.), exhibits marked association in freezing benzene. Its silver salt was analysed.
T. H. P.

Condensation Products of *m*-Methoxybenzaldehyde. HUGO BAUER and P. VOGEL (*J. pr. Chem.*, 1913, [ii], 88, 329—342).—It has been shown previously (*A.*, 1903, i, 479; 1904, i, 385; 1911, i, 881) that the introduction of alkyloxy-groups in the ortho- and para-position of the benzene nucleus in compounds of the type

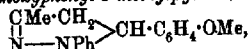


is accompanied by a marked increase in the reactivity of the bromine atom adjacent to the aromatic group; the bromine atom is readily replaced by alkyloxy-groups when the dibromides are boiled in alcoholic solution.

The reactivating influence of the alkyloxy-groups is apparently confined to the ortho- and para-positions, for the dibromides of *m*-methoxystyryl methyl ketone and phenyl *m*-methoxystyryl ketone may be boiled with alcohol without undergoing change.

m-Methoxystyryl methyl ketone, $OMe \cdot C_6H_4 \cdot CH : CH \cdot COMe$, obtained as an oil, b. p. $173^\circ/8$ mm., by the condensation of *m*-methoxybenzaldehyde with acetone in the presence of aqueous sodium hydroxide, forms a *semicarbazone*, slender, yellow needles, m. p. $197-198^\circ$, and a yellow, crystalline *phenylhydrazone*, m. p. $116-117^\circ$, which decomposes when kept and is converted by boiling in glacial acetic acid solution

into 1-phenyl-5-m-methoxyphenyl-3-methylpyrazoline,



m. p. 93—94°. It reacts with bromine (2 mols.), yielding $\alpha\beta$ -6-tri-bromo- α -3-methoxyphenylbutan- γ -one, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{COMe}$. This forms slender, white crystals, m. p. 112°, and when heated with pyridine loses hydrogen bromide with the formation of β -6-dibromo- α -3-methoxyphenyl- Δ^2 -buten- γ -one, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CH}\cdot\text{CBr}\cdot\text{COMe}$, which crystallises in extremely slender, colourless, down-like needles, m. p. 64°. The position of the bromine atom in the benzene nucleus of the preceding compounds has been established by the formation of 6-bromo-3-methoxybenzoic acid (Pechorr and others, A., 1912, i, 775) on oxidising the dibromo-compound with aqueous permanganate.

Phenyl m-methoxystyryl ketone, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COPh}$, prepared by the condensation of *m*-methoxybenzaldehyde and acetophenone in alcoholic solution by means of sodium hydroxide has b. p. 247°/12 mm., m. p. 65°, and is converted by phenylhydrazine in boiling alcoholic solution into 1:3-diphenyl-5-m-methoxyphenylpyrazoline, which crystallises in slender, green needles, m. p. 98°, yields green, fluorescent solutions in alcohol and acetone, and is oxidised by aqueous potassium permanganate to 1:3-diphenyl-5-m-methoxyphenylpyrazole, $\text{C}_{21}\text{H}_{18}\text{ON}_2$, crystallising in large, yellow needles, m. p. 140°.

It reacts with bromine in glacial acetic acid solution, yielding $\alpha\beta$ -6-tri-bromo- β -3-methoxyphenylpropionophenone (*phenyl* $\alpha\beta$ -6-tri-bromo- β -3-methoxyphenylethyl ketone), $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{COPh}$. This forms stout, colourless crystals, m. p. 140°, and is oxidised by potassium permanganate to 6-bromo-3-methoxybenzoic acid. When heated with pyridine or alcoholic ammonia, it is converted into *phenyl* α -6-dibromo-3-methoxystyryl ketone, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CH}\cdot\text{CBr}\cdot\text{COPh}$, which forms slender needles, m. p. 105°. With alcoholic sodium ethoxide it forms *phenyl* α -6-dibromo- β -ethoxy- β -3-methoxyphenylethyl ketone, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CH}(\text{OEt})\cdot\text{CHBr}\cdot\text{COPh}$,

m. p. 109—110°.

Ethyl m-methoxybenzylidenemalonate, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})_2$, prepared by maintaining a mixture of *m*-methoxybenzaldehyde and ethylmalonate, containing a little pyridine, for eight days at the ordinary temperature has m. p. 47°, b. p. 204—206°/10 mm., and is hydrolysed by aqueous sodium hydroxide to the corresponding acid, m. p. 163°, which forms a crystalline barium and amorphous silver salt, and reacts with bromine (1 mol.) in ethereal solution, yielding α -bromo- α -m-methoxyphenylmethylenemalononic acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CBr}\cdot\text{C}(\text{CO}_2\text{H})_2$, slender, yellow needles, m. p. 188°.

The ethyl ester of the last-mentioned acid is obtained as a viscid oil, b. p. 208°/10 mm., by the addition of bromine to ethyl *m*-methoxybenzylidenemalonate in glacial acetic acid.

m-Methoxybenzylidenemalononic acid reacts with bromine (2 mols.) in acetic acid solution, yielding α -6-dibromo- α -3-methoxyphenylmethylenemalononic acid, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CBr}\cdot\text{C}(\text{CO}_2\text{H})_2$, slender, pale yellow needles, m. p. 167°. When heated at 180°, it loses carbon dioxide with the formation of *m*-methoxycinnamic acid, m. p. 117° (compare Tiemann and Ludwig, A., 1883, 188), which is successively converted by the

action of bromine in glacial acetic acid solution into β -bromo-*m*-methoxycinnamic acid, slender, colourless needles, m. p. 186°, and β -6 dibromo-3-methoxycinnamic acid, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CBr}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, white needles, m. p. 160°.

6-Bromo-3-methoxybenzoic acid is readily prepared by shaking *m*-methoxybenzaldehyde with water and the theoretical amount of bromine.

If excess of bromine is used, it is accompanied by a dibromo-*m*-methoxybenzoic acid, which crystallises in slender, felted needles, m. p. 201–202°, and is separated from the monobromo-acid by taking advantage of its sparing solubility in water. F. B.

Some Acetylenic Compounds. ÉMILE ANDRÉ (*Ann. Chim. Phys.*, 1913, [viii], 29, 540–596).—The paper is mainly a résumé of work previously abstracted (A., 1910, i, 563; 1911, i, 269, 277, 545; 1912, i, 628). The following points are, however, new.

Unsuccessful attempts have been made to prepare phenylpropinene, $\text{CH}_2\text{Ph}\cdot\text{C}\equiv\text{CH}$, by the elimination of hydrogen bromide from allylbenzene dibromide.

Phenylbutinene has b. p. 189–191°/760 mm., D^{20}_D 0.9375.

isoHeptylene, b. p. 84–85°/762 mm., D^{20}_D 0.7087, is obtained by the addition of an ethereal solution of allyl iodide to a solution of magnesium isobutyl chloride in the same solvent. It unites with bromine, yielding a dibromide which, when heated with solid potassium hydroxide at about 130°, is converted into isoeptinene, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\equiv\text{CH}$, b. p. 92–93°, D^{20}_D 0.7515.

α -Propionyl- δ -phenylbutinene, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}\equiv\text{C}\cdot\text{COEt}$, is prepared by the gradual addition of a suspension of the potassium compound of δ -phenylbutinene in benzene to a solution of propionyl chloride in benzene. It is a pale yellow liquid, b. p. 162–163°/15 mm., D^{20}_D 1.0156; the piperidyl compound has m. p. 44°.

Propionylisoeptinene, b. p. 100–101°/15 mm., D^{20}_D 0.8902, is obtained in a similar manner, the benzene, however, being replaced by anhydrous ether.

ϵ -Diethylamino- β -methyl- Δ^4 -nonen- η -one, b. p. 163°/13 mm., is obtained by mixing its constituents at a low temperature.

α -Propionyl- δ -phenylbutan- β -one, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COEt}$, has b. p. 166°/13 mm., D^{20}_D 1.0460, and α -propionylisoeptan- β -one,



b. p. 106°/14 mm., D^{20}_D 0.9262.

Ethylenic β -substituted amino-ketones react with hydroxylamine in a complex manner. Thus diethylaminobenzoylstyrene yields a small

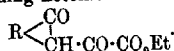
quantity of 3:5-diphenylisooxazole, $\text{O} \begin{array}{c} \diagup \text{N}=\text{CPh} \\ \diagdown \text{CPh}\cdot\text{CH} \end{array}$, m. p. 142°, together with two other substances, one of which has m. p. 163°.

Hexylphenylacetylene and isovalerylphenylacetylene react with hydroxylamine to yield 5-phenyl-3-amylisooxazole, m. p. 25–26°, b. p. 186–187°/13 mm., and 5-phenyl-3-isobutylisooxazole, b. p. 172°/13 mm., respectively, neither of which regenerates hydroxylamine when heated with dilute hydrochloric acid.

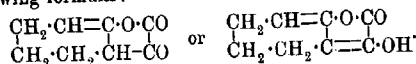
3-Phenyl-5-amylopyrazole, plates, m. p. 77—78°, is formed by the action of hydrazine on hexoylphenylacetylene.

Reduction of ethylenic β -substituted amino-ketones by sodium or sodium amalgam in alcoholic solution, or by aluminium amalgam in neutral solution, causes a quantitative separation of the amine. A regular hydrogenation of the remainder of the molecule has not yet been achieved. H. W.

Action of Ethyl Oxalate on Cyclic Ketones. ARTHUR KÖTZ and J. MEYER (*J. pr. Chem.*, 1913, [ii], 88, 261—272).—In previous papers (A., 1906, i, 88, 666, 667, 668), Kötz and others have shown that cyclic ketones condense with ethyl oxalate under the influence of sodium alkyl oxides, yielding ketonic esters of the formula



It is now found that in the case of certain derivatives of cyclohexanone, alcohol may be eliminated from the ketonic esters during the condensation, resulting in the formation of lactones derived from the following formula:

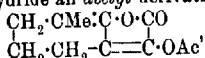


One example of the formation of a lactone of this type has already been recorded (this vol., i, 179).

From the authors' results it would appear that ketonic esters are produced when the time during which the reaction is allowed to proceed is short and the temperature low, whilst a high temperature and a more prolonged action favour the formation of lactones.

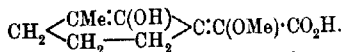
Ethyl suberone-2-oxalate (ethyl 2-cycloheptanonyl glyoxylate), prepared from cycloheptanone, ethyl oxalate, and alcoholic sodium ethoxide, has b. p. 146—148°/13 mm.

3-Methyl- Δ^2 -cyclohexen-2-ol-1-glyoxylolactone (this vol., i, 179) yields with acetic anhydride an acetyl derivative,

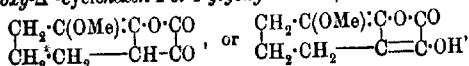


m. p. 78°.

The methyl derivative of the lactone (*loc. cit.*) is hydrolysed by aqueous potassium hydroxide (1 mol.) to 3-methylcyclohexan-2-onylidene-methoxyacetic acid, m. p. 139°, $\text{CH}_2 \begin{array}{c} \diagup \text{CHMe} \cdot \text{CO} \\ \diagdown \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C} \cdot \text{C}(\text{OMe}) \cdot \text{CO}_2\text{H}$ or

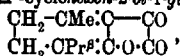


2-Methoxycyclohexanone condenses with ethyl oxalate, yielding 3-methoxy- Δ^2 -cyclohexen-2-ol-1-glyoxylolactone,



which has m. p. 51°.

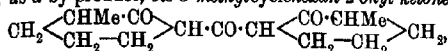
3:6-Dimethyl- Δ^2 -cyclohexen-2-ol-1-glyoxylolactone, from 1:4-dimethylcyclohexan-3-one, has m. p. 158—159°.

6-Methyl-3-isopropyl-Δ²-cyclohexan-2-ol-1-glyoxylolactone,

prepared from menthone, ethyl oxalate, and sodium in the presence of light petroleum, has m. p. 142.5° (decomp.), and decomposes on exposure to air.

In addition to ketonic esters and lactones, the condensation of ethyl oxalate with cyclohexanone and its methyl derivatives gives rise to triketones or pyrone derivatives, which are found in the higher boiling fractions of the condensation product.

Thus, the condensation of 2-methylcyclohexanone and ethyl oxalate yields, as a by-product, *bis-3-methylcyclohexan-2-onyl ketone*,

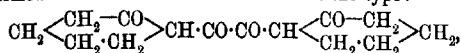


which has b. p. 170°/13 mm., and gives a reddish-violet coloration with ferric chloride.

Biscyclohexan-2-onyl ketone, from cyclohexanone, has b. p. 181°/14 mm.

3-Methylcyclohexanone yields the *pyrone* derivative, m. p. 121°, $\text{CHMe}\cdot\text{CH}_2\cdot\text{C}\cdot\text{O}\cdot\text{C}\cdot\text{CH}_2\cdot\text{CHMe}$; the *pyrone* derivative from 4-methylcyclohexanone has m. p. 91°.

The formation of the above-mentioned products is probably due to the intermediate formation of tetraketones of the type:

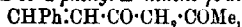


by the condensation of one molecule of the ester with two molecules of the ketone, the tetraketone being subsequently converted into the triketone and pyrone derivatives by loss of carbon monoxide and water.

F. B.

Unsaturated β-Diketones. I. HUGH RYAN and JOHN M. DUNLEA (*Proc. Roy. Irish Acad.*, 1913, 32, 1—8).—Some typical unsaturated β-diketones have been prepared by condensing cinnamic esters with saturated ketones in presence of sodium or sodamide. All attempts to prepare similar compounds by condensing acetic and benzoic esters with unsaturated ketones have, however, failed, and consequently the chief aim of the research, the formation of the parent substance of curcumin, $\text{CH}_3(\text{CO}\cdot\text{CH}\cdot\text{CHPh})_2$, from a cinnamic ester and styryl methyl ketone, could not be realised.

For the preparation of *α-phenyl-Δ²-hexene-γ₂-dione*,



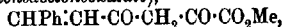
sodium wire was added during the course of some hours to a cold mixture of acetone and methyl cinnamate, and the sodium salt of the diketone was dissolved in water and decomposed by carbon dioxide. The compound crystallises in faintly yellow needles, has m. p. 83—84°, gives a yellow solution in concentrated sulphuric acid, and a red coloration with alcoholic ferric chloride, and dyes mordanted wool. On heating with hydroxylamine hydrochloride in alcohol, it yields

3-styryl-5-methylisooxazole, $\text{CHPh}:\text{CH}:\text{C} \begin{smallmatrix} \text{CH}:\text{CMe} \\ \text{N}-\text{O} \end{smallmatrix}$, which forms pearly plates from alcohol or colourless needles from light petroleum, m. p. 88°. α -Diphenyl- Δ -pentene- γ -dione, $\text{CHPh}:\text{CH}:\text{CO}:\text{CH}_2:\text{COPh}$, from acetophenone and ethyl cinnamate in the presence of sodamide, forms long, pale yellow needles, m. p. 109°, and yields 5-phenyl-3-styrylisooxazole, $\text{CHPh}:\text{CH}:\text{C} \begin{smallmatrix} \text{CH}:\text{CPh} \\ \text{N}-\text{O} \end{smallmatrix}$, in small, colourless needles, m. p. 137—138°.

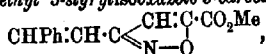
α -Phenyl- Δ -heptene- γ -dione, $\text{CHPh}:\text{CH}:\text{CO}:\text{CH}_2:\text{COEt}$, from methyl cinnamate and methyl ethyl ketone, requires a stronger acid than carbon dioxide for the decomposition of its sodium compound. It forms small, colourless prisms, which soften at 154° and melt to a yellow liquid at 161—163°. Similarly, α -phenyl- Δ -isooctene- γ -dione, $\text{CHPh}:\text{CH}:\text{CO}:\text{CH}_2:\text{CO}:\text{CHMe}_2$, crystallises in thin plates which are probably rhombic, and softens at 165° and melts to a yellow liquid at 173—175°. These diketones are soluble in potassium hydroxide, but do not give coloured solutions in sulphuric acid or colorations with ferric chloride, nor do they dye mordanted wool. That their constitution is not represented by the alternative formulæ was proved by methylating α -phenyl- Δ -hexene- γ -dione, when it was found that α -phenyl- δ -methyl- Δ -hexene- γ -dione, $\text{CHPh}:\text{CH}:\text{CO}:\text{CHMe}:\text{COMe}$, was not identical with the above α -phenyl- Δ -heptene- γ -dione, but formed long, pale yellow needles, m. p. 88—89°, and gave a dark brown coloration with alcoholic ferric chloride, a yellow solution in sulphuric acid, and a pale brown colour to wool mordanted with iron.

J. C. W.

Unsaturated β -Diketones. II. HUGH RYAN and JOSEPH ALGAR (*Proc. Roy. Irish Acad.*, 1913, 32, 9—16).—Although unsaturated ketones did not yield definite compounds on condensation with acetic or benzoic esters (compare preceding abstract), such a result has been attained with the oxalic esters. Methyl α -diketo- ϵ -phenyl- Δ^3 -hexenoate (methyl benzylideneacetoneoxalate),



from styryl methyl ketone and methyl oxalate in the presence of sodium, forms pale yellow, acicular prisms, m. p. 70° (compare the ethyl ester, Schiff and Gigli, A., 1898, i, 490). It gives a yellow solution in potassium hydroxide, an orange solution in concentrated sulphuric acid, and a yellow solution with greenish fluorescence in alcohol. Ferric chloride imparts a dark red colour to an alcoholic solution, and the substance dyes wool orange-red or brown, according to the mordant employed. α -Diketo- ϵ -phenyl- Δ^3 -hexenoic acid, $\text{CHPh}:\text{CH}:\text{CO}:\text{CH}_2:\text{CO}:\text{CO}_2\text{H}$, may readily be obtained by hydrolysis of the ester, in pale yellow needles, m. p. 139—140°. When the methyl ester is heated with hydroxylamine hydrochloride in methyl alcohol, methyl 3-styrylisooxazole-5-carboxylate,



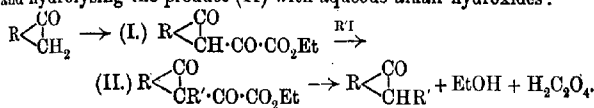
is formed in long, colourless needles, m. p. 142—143°. When ethyl

alcohol is employed, however, a transformation occurs, and the *ethyl* ester is produced, in colourless crystals, m. p. 111°. The free acid, $C_{15}H_{19}O_5N$, is white, and has m. p. 190—192°. The above methyl ester also absorbs bromine, yielding *methyl δ-dibromo-α-diketo-ε-phenylhexoate*, $CHPhBr \cdot CHBr \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Me$, in almost colourless prisms, m. p. 134°.

Similar compounds were obtained by condensing *p*-methoxystyryl methyl ketone with methyl oxalate. *Methyl α-diketo-ε-p-methoxyphenyl-Δδ-hexoate*, $OMe \cdot C_6H_4 \cdot CH:CH \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Me$, forms yellow needles, m. p. 127.5°, and with bromine yields *methyl δ-dibromo-α-diketo-ε-p-methoxyphenylhexoate*, $C_{14}H_{14}O_5Br_2$, in pale yellow needles, m. p. 106—108° (decomp.). The free acid crystallises with water in bright yellow, slender needles, whilst the anhydrous substance is deep orange, and has m. p. 150—151°. *Ethyl 3-p-methoxystyryl-isooxazole-5-carboxylate*, $C_{18}H_{15}O_4N$, from the above methyl ester with hydroxylamine hydrochloride in ethyl alcohol, forms long, colourless needles, m. p. 76—77°.

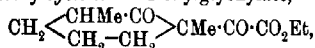
J. C. W.

Alkylation of Ketones by means of β-Ketoneoxalic Esters.
ARTHUR KÖTZ and K. BLENDERMANN (*J. pr. Chem.*, 1913, [ii], 88, 257—260).—The method previously employed (this vol., i, 179) to convert 1-methylcyclohexan-3-one into 1:4-dimethylcyclohexan-3-one is found to be of general application for alkylating both aliphatic and hydroaromatic ketones. It consists in condensing the ketone with ethyl oxalate by means of sodium methoxide or ethoxide, heating the sodium derivative of the resulting ketonic ester (I) with an alkyl halide, and hydrolysing the product (II) with aqueous alkali hydroxides:



Thus, acetone can be converted into methyl ethyl ketone by condensing it with ethyl oxalate and alcoholic sodium ethoxide, heating the ethyl sodioacetoneoxalate thus formed with methyl iodide, and hydrolysing the resulting methyl derivative with the calculated amount of 10% aqueous sodium hydroxide.

Ethyl 1:3-dimethylcyclohexan-2-onylglyoxylate,



obtained from 1-methylcyclohexan-2-one, ethyl oxalate, and methyl iodide, yields, on hydrolysis, 1:3-dimethylcyclohexan-2-one (Kötz and Schaeffer, A., 1912, i, 603).

On treatment with ethyl iodide and subsequent hydrolysis, the sodium derivative of ethyl 4-methylcyclohexan-2-onylglyoxylate, obtained from 1-methylcyclohexan-3-one and ethyl oxalate, yields 1-methyl-4-methylcyclohexan-3-one, a strongly refractive, colourless liquid, b. p. 81—82°/17 mm., having an odour resembling that of menthone.

4-Benzyl-1-methylcyclohexan-3-one, prepared in a similar manner, using benzyl chloride, has b. p. 176°/15 mm.

Ethyl methylisobutyronoxalate (ethyl 1:3:4-trimethyl-5-isopropyl-Δ³-

cyclohexen-2-onyl glyoxylate), $\begin{matrix} \text{CMe} \text{---} \text{CO} \\ | \\ \text{CMe} \cdot \text{CHPr}^s \end{matrix} > \text{CMe} \cdot \text{CO} \cdot \text{CO} \cdot \text{Et}$, obtained by heating the product of the condensation of isothujone and ethyl oxalate with methyl iodide, has b. p. $183^\circ/11 \text{ mm.}$, and is hydrolysed by aqueous sodium hydroxide to methylisothujone (1:3:4-trimethyl-5-isopropyl- Δ^2 -cyclohexen-2-one), $\begin{matrix} \text{CMe} \text{---} \text{CO} \\ | \\ \text{CMe} \cdot \text{CHPr}^s \end{matrix} > \text{CHMe}$, which has b. p. $229\text{--}231^\circ$, and has also been prepared by the reduction of hydroxymethyleneisothujone (Schaeffer, *Diss.*, Göttingen, 1903). F. B.

Isolation of Lapachol from the Heart-wood of *Avicennia tomentosa*. KONRAD BOURNOT (*Arch. Pharm.*, 1913, 251, 351—354). —The residue left after the evaporation of the ethereal extract of the powdered heart-wood of *Avicennia tomentosa* yields to 3% aqueous sodium carbonate a substance, lapachol, $\text{C}_{15}\text{H}_{14}\text{O}_8$, m. p. $140\text{--}141^\circ$, truncated, yellow plates, which is shown by its m. p., crystalline form, solubilities, and formation of a diacetyl derivative, m. p. 130° , to be identical with Paternò's and with Hooker's lapacholic acid (2-hydroxy-3-*ow*-dimethylallyl- α -naphthaquinone). C. S.

The Anthraquinone Series. I. Halogenated 2-Aminoanthraquinones. WALTER JUNGHEANS (*Annalen*, 1913, 399, 316—330). —1-Chloro-2-acetylaminanthraquinone, m. p. $241\text{--}242^\circ$ (corr.), faintly yellow needles, obtained by the chlorination of 2-acetylaminanthraquinone in acetic acid containing sodium acetate on the water-bath, yields, by hydrolysis by acids or alkalis, 1-chloro-2-aminoanthraquinone, m. p. 237° , orange needles or reddish-brown leaflets. The latter reacts with *p*-toluenesulphonamide, potassium acetate, and a trace of copper acetate in boiling amyl alcohol to form 1-*p*-toluenesulphonylamino-2-aminoanthraquinone, m. p. 239° (corr.), yellowish-red leaflets. In a similar manner, 1-chloro-2-acetylaminanthraquinone yields 1-*p*-toluenesulphonylamino-2-acetylaminanthraquinone, m. p. 207° (corr.), long needles. Both of these substances yield 1:2-diaminoanthraquinone by hydrolysis, whereby the constitution of the chloroaminoanthraquinones is determined.

By treatment with chlorine in warm glacial acetic acid or with potassium chlorate and concentrated hydrochloric acid in glacial acetic acid at the ordinary temperature, 2-aminoanthraquinone yields 1:3-dichloro-2-aminoanthraquinone, m. p. 231° (corr.), yellowish-brown needles, which is converted by boiling acetic anhydride into 1:3-dichloro-2-diacetylaminanthraquinone, m. p. 199° (corr.), silvery leaflets, and into 1:3-dichloro-2-benzoylaminoanthraquinone, m. p. 227° (corr.), faintly yellow needles, by benzoyl chloride in boiling nitrobenzene. The constitution of 1:3-dichloro-2-aminoanthraquinone is proved by eliminating the amino-group in the usual manner, whereby is obtained the 1:3-dichloroanthraquinone, m. p. 203° (corr.), which is produced from 1:3-dichloro-4-aminoanthraquinone by the same method.

Contrary to statements in the literature, the interaction of equal molecular quantities of 2-aminoanthraquinone and bromine in glacial acetic acid at the ordinary temperature produces 3-bromo-2-amino-

anthraquinone hydrobromide, from which the *base*, m. p. 311° (corr.), yellow leaflets, is obtained by boiling with water. 3-Bromo-2-aminoanthraquinone forms an *acetyl* derivative, m. p. 217° (corr.), colourless needles, and a *benzoyl* derivative, m. p. 279° (corr.), colourless needles. Its constitution is proved by deamidation, whereby 2-bromoanthraquinone is produced, and also by the formation of a thiazole derivative (Ullmann and Junghans, below). By prolonged boiling with glacial acetic and concentrated hydrobromic acids, 1:3-dibromo-2-aminoanthraquinone loses the halogen atom in position 1 and yields 3-bromo-2-aminoanthraquinone, m. p. 311° (corr.). C. S.

Preparation of β -Bromoaminoanthraquinones Containing a Bromine Atom in the Next Position to an Amino-group. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 261270 and 261271).—3-Bromo-2-aminoanthraquinone, m. p. 305° , as previously obtained (A., 1904, i, 512) had m. p. 267° — 270° , and the pure substance has now been prepared as follows: 2-aminoanthraquinone (5.8 parts) and 10 parts of 1:3-dibromo-2-aminoanthraquinone (A., 1905, i, 797) dissolved in 160 parts of concentrated sulphuric acid are slowly heated with continual stirring to 160° , when a reaction takes place, and after about fifteen minutes at 170° pure 3-bromo-2-aminoanthraquinone sulphate crystallises out; the same result is obtained if the bases are heated together during ten minutes at 280° in the absence of any solvent.

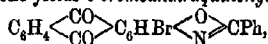
2-Bromo-1-aminoanthraquinone (A., 1905, i, 910) is obtained in a similar manner from 1-aminoanthraquinone and 2:4-dibromo-1-aminoanthraquinone.

1:3:5:7-Tetrabromo-2:6-diaminoanthraquinone, yellowish-brown needles, m. p. above 360° , is prepared by brominating an aqueous suspension of 2:6-diaminoanthraquinone, and when molecular proportions of these two bases are heated together at 195° in slightly diluted sulphuric acid during half an hour, they furnish pure 3:7-dibromo-2:6-diaminoanthraquinone sulphate; whilst a mixture of 1:5-diamino- and 2:4:6:8-tetrabromo-1:5-diaminoanthraquinones gives rise to 2:6-dibromo-1:5-diaminoanthraquinone (A., 1905, i, 88).

II. States that 3-bromo-2-aminoanthraquinone can be prepared in one operation by dissolving 2-aminoanthraquinone in concentrated sulphuric acid, cooling, and treating with bromine (1 mol.); the crude mixture, which contains monobromo-, dibromo-, and unbrominated bases, is then heated at 180° — 190° , when it furnishes entirely 3-bromo-2-aminoanthraquinone. In a similar manner, 2:7-diaminoanthraquinone when treated with bromine (2 mols.) gives rise to 3:6-dibromo-2:7-diaminoanthraquinone; this compound closely resembles 3:7-dibromo-2:6-diaminoanthraquinone, but is more readily soluble in organic liquids. F. M. G. M.

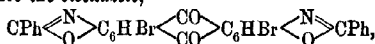
The Anthraquinone Series. II. 1:3-Dibromo-2-aminoanthraquinone. FRITZ ULLMANN and WALTER JUNGHANS (*Annalen*, 1913, 399, 330—345).—The following reactions illustrate the great mobility, in the presence of a copper salt as catalyst, of the halogen

atom in position 1 in 1:3-dibromo-2-aminoanthraquinone (compare Ullmann and Medenwald, this vol., i, 735). By boiling with benzoyl chloride and nitrobenzene, or with benzoic anhydride, 1:3-dibromo-2-aminoanthraquinone yields 3-bromoanthraquinonylphenyloxazole,



m. p. 325° (corr.), yellow leaflets, which is decomposed by boiling 80% sulphuric acid, forming, after the addition of water, 3-bromo-2-amino-1-hydroxyanthraquinone, m. p. 269°, reddish-brown needles. 1:3-Dibromo-2-dibenzoylaminoanthraquinone, m. p. 233°, yellow needles, is also obtained by the first method of preparing the oxazole derivative.

In a similar manner, 1:3:5:7-tetrabromo-2:6-diaminoanthraquinone, by boiling with benzoyl chloride and naphthalene, is converted into the bisoxazole,

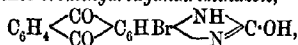


m. p. above 360°, faintly yellow needles.

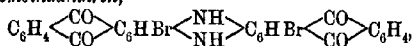
By boiling with amyl alcohol, anhydrous potassium acetate, a little copper acetate, and *p*-toluenesulphonamide, 1:3-dibromo-2-aminoanthraquinone is converted into 3-bromo-2-amino-1-*p*-toluenesulphonylaminoanthraquinone, $\text{C}_{21}\text{H}_{15}\text{O}_4\text{N}_2\text{BrS}$, m. p. 237.5° (corr.), yellowish-brown crystals, which yields 3-bromo-1:2-diaminoanthraquinone, m. p. 312° (corr.), dark red crystals, by hydrolysis with sulphuric acid. By boiling 3-bromo-1:2-diaminoanthraquinone with benzaldehyde or 3-bromo-2-amino-1-*p*-toluenesulphonylaminoanthraquinone with benzoyl chloride,

the iminoazole, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{HBr} \begin{array}{c} \diagup \text{N} \diagdown \\ \diagdown \text{NH} \diagup \end{array} \text{CPh}$, m. p. 292° (corr.), yellowish-green needles, is obtained, which forms a hydrochloride, colourless needles, and a reddish-brown sodium salt.

In the presence of anhydrous sodium acetate and a trace of copper acetate, 1:3-dibromo-2-aminoanthraquinone is converted by urethane on the water-bath into bromohydroxyanthriminazole,



m. p. 370°, yellowish-green needles, and by boiling nitrobenzene into 3:3'-dibromoindanthren,



m. p. 515°, indigo-blue needles, and 3-bromo-2-aminoanthraquinone; the dibromoindanthren forms a blue vat which dyes cotton in blue shades.

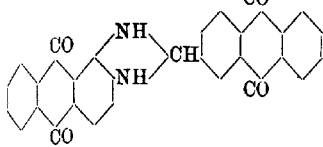
1:3-Dibromo-2-aminoanthraquinone and boiling benzaldehyde yield a benzylidene derivative, $\text{C}_{21}\text{H}_{11}\text{O}_3\text{NBr}_2$, m. p. 195° (corr.), yellowish-green needles, which is converted by naphthalene and copper powder at 240—245° into 3:3'-dibromo-2:2'-dibenzylideneamino-1:1'-di-anthraquinonyl, $\text{C}_{42}\text{H}_{22}\text{O}_4\text{N}_4\text{Br}_2$, m. p. 295.5° (corr.), yellow leaflets. By treating the latter in hot nitrobenzene with a little sulphuric acid, or 3-bromo-2-aminoanthraquinone in boiling nitrobenzene with antimony pentachloride, 3:3'-dibromostavanthren, $\text{C}_{28}\text{H}_{10}\text{O}_2\text{N}_2\text{Br}_2$, m. p. 495°, brown needles, is obtained; its hyposulphite vat is deep blue and dyes cotton in the same shades, changing to orange in air. C. S.

[Preparation of a Bromo-derivative of 4-Chloro-1-methyl-anthraquinone.]—FARBWERKE vorm. MEISTER, LUCIUS & BRÜNING (D.R.-P. 259881).—When a boiling nitrobenzene solution of 4-chloro-1-methylanthraquinone (15 parts) is treated with a similar solution of bromine (8.5 vols.) it furnishes a compound which separates in orange crystals as the solution cools; the m. p. is above 300°.

F. M. G. M.

Preparation of Condensation Products in the Anthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 261737).

—The compound (annexed formula) is obtained when 1:2-diaminoanthraquinone and anthraquinone-2-aldehyde are heated together in pyridine solution at 120°; the aldehyde can be replaced in this reaction by ω -chloro- or ω -dichloromethylanthraquinones, and the diamine by 2:3-diaminoanthraquinone.



F. M. G. M.

[Preparation of Anthraquinone Derivatives.] FARBWERKE vorm. MEISTER, LUCIUS & BRÜNING (D.R.-P. 262252).—4- α -Anthraquinonylaminoanthraquinone-1:2-acridone is obtained by condensing 4-aminoanthraquinoneacridone with α -chloroanthraquinone in the presence of aluminium chloride, zinc chloride, or sulphuric acid.

F. M. G. M.

Preparation of Condensation Products in the Anthracene Series. FARBWERKE vorm. MEISTER, LUCIUS & BRÜNING (D.R.-P. 260662).

—The removal of chlorine or bromine by means of potassium iodide and acetone has previously been described (A., 1911, i, 432), and it is now found that when ω -dibromo-2-methylanthraquinone is heated with potassium iodide (2 parts) and acetone (10 parts) at 100° during twelve to fourteen hours, it yields the previously-described compound, $C_{20}H_{14}O_4$ (A., 1908, i, 999).

When $\omega\omega'$ -tetrabromo-2:2'-dimethyl-1:1'-dianthraquinonyl (A., 1912, i, 361) is treated in a similar manner, it gives rise to a di-phthaloylphenanthren, an orange-brown powder; the preparation of other derivatives by this reaction is discussed.

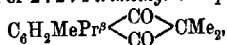
F. M. G. M.

Synthesis of the Higher Indandiones. II. MARTIN FREUND and KARL FLEISCHER (*Annalen*, 1913, 399, 182—241).—The reaction whereby diethylmalonyl chloride and benzene or its homologues yield diethylindandiones (A., 1910, i, 490) has been examined in the cases where dimethylmalonyl chloride or dipropylmalonyl chloride is used.

[With MARGARETE DECKERT.]—Dimethylmalonyl chloride, which is identified in small quantities best by conversion into dimethylmalonanilide, $CM_2(CO \cdot NHPh)_2$, m. p. 202.5—203°, reacts abnormally with benzene in the presence of aluminium chloride, yielding ultimately phenyl isopropyl ketone and two substances, $C_{17}H_{16}O_2$, m. p. 193—194°

and 125° respectively, which are probably $\beta\beta$ -dibenzoylpropane and the lactone of β -hydroxy- $\beta\beta$ -diphenyl- $\alpha\alpha$ -dimethylpropionic acid; the two substances have not been further examined on account of the difficulty of separating them.*

Dimethylmalonyl chloride condenses normally with other aromatic hydrocarbons, yielding substituted indandiones. Thus its reaction with *p*-cymene in carbon disulphide in the presence of aluminium chloride leads to the formation of 2:2:4-trimethyl-7-isopropylindandione,



b. p. 168—169°/14 mm., D^{15}_D 1.634, which is oxidised to an acid, probably $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_2 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CMe}_2$, m. p. 179—180°, by nitric acid at 115—140°.

Under conditions similar to the preceding, dimethylmalonyl chloride and naphthalene ultimately yield three substances, $\text{C}_{15}\text{H}_{10}\text{O}_2$, m. p. 101°, 121°, and 137° respectively, which can only be separated by the mechanical sorting of their well-defined crystals. The constitutions of the three substances have been determined by oxidising the products of their decomposition by alkalis. The substance, m. p. 101°, is

2:2-dimethyl-1:8-naphthindandione, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CMe}_2$, since it is con-

verted by boiling 50% potassium hydroxide into 1-isobutyrylnaphthalene-8-carboxylic acid, $\text{CHMe}_2\cdot\text{CO}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$, m. p. 158.5—159.5°, hexagonal plates and prisms, which is oxidised to naphthalic anhydride by nitric acid at 125°. The substance, m. p. 121°, is 2:2-dimethyl-1:2-

naphthindandione, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CMe}_2$; it is converted by 50% potassium

hydroxide into 1(or 2)-isobutyrylnaphthalene-2(or 1)-carboxylic acid, m. p. 153—154°, which is oxidised to naphthalene-1:2-dicarboxylic acid and its anhydride by boiling glacial acetic acid and nitric acid, D 1.4. The third substance, m. p. 137°, must be 2:2-dimethyl-2:3-naphthindandione by exclusion; it is converted by alkali into 2-isobutyrylnaphthalene-3-carboxylic acid, m. p. 164—165.5°, which is oxidised to naphthalene-2:3-dicarboxylic acid, m. p. 241° (decomp.), by nitric acid at 120°, or by boiling nitric and glacial acetic acids. Naphthalene-2:3-dicarboxylic acid forms an anhydride, m. p. 245°, by heating, and yields a fluorescein by the usual method.

By direct treatment with nitric acid at 120—140° 2:2-dimethyl-1:8-naphthindandione yields a nitro-derivative, $\text{C}_{15}\text{H}_{11}\text{O}_4\text{N}$, m. p. 162°, yellow needles; a dinitro-derivative, $\text{C}_{15}\text{H}_9\text{O}_6\text{N}_2$, m. p. 245—248° (decomp.), microscopic, hexagonal plates or prisms, and a colourless acid, m. p. 237—239° (decomp.); 2:2-dimethyl-1:2-naphthindandione yields a yellow substance containing nitrogen, and an acid, $\text{C}_{13}\text{H}_{10}\text{O}_4$, m. p. 229—233° (decomp.), which is probably 2:2-dimethylindandione-

4:5-dicarboxylic acid, $\text{CMe}_2 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C}_6\text{H}_3(\text{CO}_2\text{H})_2$, whilst 2:2-dimethyl-

2:3-naphthindandione yields nitrogenous products and a substance, m. p. 186—187° (decomp.), colourless needles.

When heated above their m. p.'s, 1-isobutyrylnaphthalene-8-carboxylic acid and 2-isobutyrylnaphthalene-3-carboxylic acid are converted

into lactones, $C_{10}H_6 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{:CMe}_2) \end{smallmatrix} O$, m. p. 117.5—118.5° and 174—175° respectively, which are isomeric with the original indandiones; the former lactone is re-converted into 1-isobutyrylnaphthalene-8-carboxylic acid by boiling 50% potassium hydroxide, is oxidised to naphthalic anhydride by boiling nitric and glacial acetic acids, and yields a bromo-derivative, m. p. 141°, microscopic prisms, by bromination in chloroform. 1(or 2)-isobutyrylnaphthalene-2(or 1)-carboxylic acid remains unchanged by heating above its m. p.

Assuming that the $-\text{CH}_2 \cdot \text{CH}_2-$ group is unattacked, acenaphthene could yield three indandiones by reaction with dimethylmalonyl chloride and aluminium chloride in carbon disulphide. Actually only two are obtained, having m. p. 127.5—129° and 176.5—177.5° respectively. The former crystallises in colourless needles, and is 2:2-dimethyl-

3:4-acenaphthindandione, $\text{CMe}_2 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} C_{10}H_4 \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix}$, since it is converted by boiling 50% potassium hydroxide into 3-isobutyrylacenaphthene-4-carboxylic acid, $\begin{smallmatrix} \text{CO}_2\text{H} \\ \diagup \quad \diagdown \\ \text{CHMe}_2 \cdot \text{CO} \end{smallmatrix} C_{10}H_4 \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix}$, m. p. 176° (decomp.), colourless, microscopic plates, which is oxidised to naphthalene-1:4:5:8-tetracarboxylic acid by alkaline potassium permanganate. The isomeride, m. p. 176.5—177.5°, crystallises in pale yellow needles, and is named dimethylisoacenaphthindandione; its formula has not been definitely determined.

The oxidation of 2:2-dimethyl-3:4-acenaphthindandione by sodium dichromate and boiling glacial acetic acid yields 2:2-dimethyl-1:8-naphthindandione-4:5-dicarboxylic acid, $\text{CMe}_2 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} C_{10}H_4(\text{CO}_2\text{H})_2$, m. p. 208—209° (anhydride, m. p. 207—208°).

When heated above its m. p., 3-isobutyrylacenaphthene-4-carboxylic acid is converted into a lactone, $\begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} C_{10}H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{:CMe}_2) \end{smallmatrix} O$, m. p. 175—176°, orange needles, which is oxidised by boiling acetic and nitric acids to acenaphthalic anhydride (anhydride of acenaphthene-3:4-dicarboxylic acid), $\begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} C_{10}H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} O$, m. p. 293—294°, pale brown leaflets. Acenaphthalic acid forms an ammonium salt, m. p. 283°, yields its anhydride by heating, does not form a fluorescein, and dissolves in concentrated sulphuric acid, yielding a pale yellow solution with a splendid sky-blue fluorescence.

The reaction between anthracene and an excess of dimethylmalonyl chloride in the presence of aluminium chloride leads to the formation of 2:2-dimethylanthraceneindandione, $C_6H_4 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} C_6H_2 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CMe}_2$, m. p. 148.5—149.5°, brownish-red needles or plates, which is oxidised by chromic and acetic acids to 2:2-dimethylanthraquinoneindandione, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} C_6H_2 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CMe}_2$, m. p. 231—232°, pale yellow prisms, and is converted by boiling 50% potassium hydroxide into an isobutyryl-

anthracene-*o*-carboxylic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{C}_6\text{H}_2(\text{CO}_2\text{H}) \cdot \text{COPr}^a$, m. p. 203—205°, dark brown prisms; the latter, heated above its m. p., is converted into a lactone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{CMe}_2) \end{smallmatrix} \text{O}$, m. p. 141—142.5°.

Dimethylmalonyl chloride and phenanthrene in carbon disulphide in the presence of aluminium chloride yield ultimately a *dimethylphenanthreneindandione*, m. p. 207—208°, pale yellow needles, which is converted into *dimethylphenanthraquinoneindandione*, $\text{C}_{10}\text{H}_{12}\text{O}_4$, m. p. 246—247°, orange needles, by oxidation, and into a mixture of two isomeric acids by concentrated potassium hydroxide.

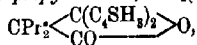
[With MAX ROTHSCHILD.]—Dipropylmalonyl chloride is characterised by conversion into the *dianilide*, $\text{CPr}_2(\text{CO} \cdot \text{NHPh})_2$, m. p. 168—168.5°, colourless prisms, and the *bisphenylhydrazide*, $\text{C}_{21}\text{H}_{28}\text{O}_2\text{N}_4$, m. p. 216—217°; by warming with carbonyl chloride in toluene at 100°, the latter is converted into the *diazolone*, $\begin{smallmatrix} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{NPh} \cdot \text{N} \end{smallmatrix} \text{C} \cdot \text{CPr}_2 \cdot \text{C} \begin{smallmatrix} \text{O} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{NPh} \end{smallmatrix}$, m. p. 157—158.5°.

Dipropylmalonyl chloride condenses normally with benzene or other aromatic hydrocarbons in the presence of aluminium chloride. Thus benzene yields, in addition to a small quantity of *88-dibenzoyltheptane*,

m. p. 106—107°, 2:2-*dipropylindandione*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CPr}_2$, b. p. 168—172°/14 mm., D 1.0390, which is converted into phthalic acid by oxidation. *p*-Cymene yields 4-*methyl-2:2-dipropyl-7-isopropylindandione*, $\text{C}_6\text{H}_4\text{MePr}^a \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CPr}_2$, m. p. 94.5°, colourless needles.

Diphenyl yields a *phenyldipropylindandione*, $\text{C}_{21}\text{H}_{22}\text{O}_2$, m. p. 221.5°, colourless needles, the constitution of which has not been definitely determined. Naphthalene does not yield definite condensation products, but acenaphthene yields two *isomerides*, m. p. 154—154.5° and 126° respectively. The former crystallises in yellow needles, and is converted by boiling concentrated aqueous alkalis, or, better, by sodium and boiling alcohol into *a-propylvalerylacenaphthene-carboxylic acid*, $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} \text{C}_{10}\text{H}_4(\text{CO}_2\text{H}) \cdot \text{CO} \cdot \text{CHPr}_2$, m. p. 166—167°, yellowish-brown leaflets. The isomeride, m. p. 126°, crystallises in yellow leaflets, and does not yield definite products by decomposition by alkalis.

Dipropylmalonyl chloride yields oily or amorphous products with anthracene, phenanthrene, and retene, but condenses with thiophen in the presence of aluminium chloride and carbon disulphide to form ultimately *dithiophenoyldipropylmethane*, $\text{CPr}_2(\text{CO} \cdot \text{C}_4\text{SH}_3)_2$ or

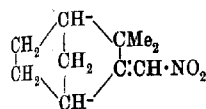


m. p. 192.5°, yellow needles, and *thiophenoyldipropylmethane*, $\text{C}_{12}\text{H}_{18}\text{OS}$, b. p. 158—163°/25 mm.

A table is given of the colours of the fluorescent solutions of the preceding substances in concentrated sulphuric acid. C. S.

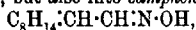
Action of Nitrogen Trioxide on Camphene. Nitrocamphene and Dinitrohydroxycamphane. PETER LIPP (*Annalen*, 1913, 399, 241—260).—By the oxidation of *isocamphane* by nitric acid the author obtained (A., 1911, i, 731), amongst other products, a substance, $C_{10}H_{15}O_2N$, m. p. 64° , which is identical with so-called camphenile nitrite obtained by Jagelki by the action of nitrogen trioxide on camphene. The author's opinion that the substance is a nitro-compound (*loc. cit.*) has now been confirmed. He has, therefore, re-examined the action of nitrogen trioxide on camphene.

l-Camphene in petroleum (b. p. $30-40^\circ$) at -16° is treated with nitrogen trioxide (from arsenious oxide and nitric acid, not from sodium nitrite), whereby a faintly olive-green oil is produced, which decomposes at the ordinary temperature. The solvent is removed and the oily residue, after distillation with steam, is treated with aqueous potassium hydroxide. The deep red alkaline solution is treated as described below, whilst the residue is the desired substance, *l*-nitro-

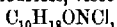


camphene (annexed formula), m. p. $84-85^\circ$ (corr.), $[\alpha]_D^{20} = -146.4^\circ$ in 20% benzene solution, which only differs from *dl*-nitrocamphene, m. p. 64° , in its m. p. and optical activity. The evidence for the presence of a nitro-group is the following: (i) The faintly yellow colour of the substance may be due to

the presence of the nitro-group in the neighbourhood of the double linking. (ii) By treatment with alcoholic ammonia at $110-120^\circ$, the substance is converted into *l*-camphenilone and nitromethane (identified in the form of methylamine); by the action of boiling, aqueous alcoholic potassium hydroxide, the substance yields *l*-camphenilone and potassium nitroacetate. The nitro-group, therefore, is attached directly to a carbon atom. (iii) By reduction in ethereal solution by aluminium amalgam and water, the substance is converted into, not only ammonia and camphenilaldehyde (which are the products of reduction in acid or in alkaline solution), but also into *camphenilalaldoxime*,



b. p. $134-135^\circ/12 \text{ mm.}$, a colourless, viscous liquid (*hydrochloride*,

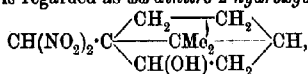


m. p. $90-92^\circ$, white, crystalline powder). The formation of camphenilalaldoxime is quite analogous to the production of aldoximes by the reduction of nitro-olefines in neutral solution. (iv) The conversion of nitrocamphene into tricyclic acid by concentrated sulphuric acid is to be described fully in a future communication. The first product is a *sulphate* of camphenylhydroxamic acid, $C_{10}H_{15}O_3NS$, decomp. 127° ; this is decomposed by warm water into sulphuric acid and *camphenylhydroxamic acid*, $C_{10}H_{17}O_3N$, decomp. 163° . The latter is decomposed by sulphuric acid into hydroxylamine and camphenylic acid, and from the latter, by loss of water, tricyclic acid is produced. The whole change is analogous to the conversion of a primary nitro-compound into a carboxylic acid containing the same number of carbon atoms.

A second product of the action of nitrogen trioxide on camphene is the oily substance, $C_{10}H_{16}O_2N_2$, described by Jagelki as camphene

nitrosite. However, the substance, the *potassium* salt, $C_{10}H_{15}O_4N_2K$, garnet prisms or bronze leaflets, decomp. $207-209^\circ$, of which is contained in the deep red alkaline solution mentioned above, is, when pure, crystalline, m. p. 158.5° (corr.), and has the formula $C_{10}H_{16}O_5N_2$.

The substance is regarded as *ω-dinitro-2-hydroxycamphane*,



for the following reasons: The presence of the hydroxyl group is shown by the formation of an *acetyl* derivative, $C_{12}H_{18}O_6N_2$, m. p. $74-75^\circ$ (corr.), stout plates. The substance, as a secondary alcohol, is oxidised to ketopinic acid by alkaline potassium permanganate at $50-60^\circ$. The presence of a *gem*-dinitro-group is suggested by the intense red colour of the potassium salt and by its reconversion into the colourless parent substance by carbon dioxide, and is confirmed by the reduction of an ethereal solution of the substance by aluminium amalgam and water, whereby hydroxylamine and an *oxime*, $C_{10}H_{17}O_4N$, m. p. $127-128.5^\circ$, colourless needles, are produced; the oxime is probably *2-hydroxycamphane-ω-aldoxime*, $C_8H_{15}O:C:CH:OH$, but the aldehyde obtained from it has not been thoroughly examined owing to lack of material.

The formation of a camphane derivative, *ω-dinitro-2-hydroxycamphane*, from camphene by the action of nitrogen trioxide is effected possibly by the intermediate production of nitrocamphene. This view, however, is not altogether supported by the fact that nitrocamphene and nitric acid, D 1.514, after being kept for four days yield a substance which dissolves in alkalis with a deep red colour, but cannot be isolated, the chief product of the reaction being ketopinic acid, (*p-bromophenylhydrazone*, $C_{16}H_{19}O_5N_2Br$, m. p. $165-166^\circ$ (corr.), straw-yellow leaflets). Possibly the nitrocamphene and the nitrous acid in the nitric acid form a nitrolic acid, the camphene ring changing at the same time to the camphane ring; the nitrolic acid is then oxidised to ketopinic acid. Attempts to unite nitrocamphene and nitrous acid directly have been unsuccessful.

C. S.

Action of Methyl Iodide and Magnesium on Menthone. ALEXANDER E. ARBUZOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 700).—The author claims priority for Zelinsky (A., 1901, i, 660) and himself (A., 1908, i, 555) over Vanin (A., 1912, i, 788).

T. H. P.

Oil of Adansonia Grandidieri. VICTOR THOMAS and F. BOLT (*Bull. Soc. chim.*, 1913, [iv], 13, 827-832).—On extraction with ether, the entire seeds of *Adansonia Grandidieri* yield 43% of oil, whilst the decorticated seeds give 64.5%. The oil obtained from the former has m. p. $20-21^\circ$; temperature of solidification, 13° ; D^{20}_4 0.9190; n^{40}_D 1.4585; saponification number, 192.4; iodine number, $65.4-66.1$; Reichert-Meissl number, 0.77; Hehner number, 95.5, whilst that obtained from the latter has m. p. $39-40^\circ$; temperature of solidification, 33° ; D^{40}_4 0.9135; n^{40}_D 1.4521; saponification number, 196; iodine number, 36.9. After removal of the fatty acids, the oils from the entire (i) and decorticated seeds (ii) have the following constants:

m. p. (i) 51—52°; (ii) 45—46°; temperature of solidification, (i) 44·5°; acid number, (i) 179; (ii) 204·5; saponification number, (i) 202·5; (ii) 207·6; iodine number, (i) 66·3—66·9; (ii) 34·5—35; iodine number after acetylation, (i) 25·7; (ii) 26·8.

The oil consists of a mixture of esters of solid and unsaturated liquid acids in the proportion of 42% of the former and 58% of the latter. It is further characterised by the presence of a considerable quantity of a lactone, the precise nature of which has not been determined owing to lack of material. It has an iodine number 67·2, and when treated with bromine yields a liquid bromo-derivative.

The mixture of acids contains myristic acid, 7·6%; palmitic acid, 32·5%; oleic acid, 36·5%; linoleic acid, 8·7%, and lactone, 11·41%.

H. W.

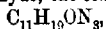
Essential Oils. V. Essence of Cypress. GUSTAVE LALOUZE (*Bull. Soc. chim.*, 1913, [iv], 13, 752—754. Compare A., 1911, i, 138; 1912, i, 574, 636).—The author has studied the oils obtained from the branches of *Cupressus sempervirens fastigiata*, L., and *Cupressus lusitanica*, Mill. The latter species yields rather more oil than the former. The oil from the former is brownish, and has D_{15}^{20} 0·8744; n_D^{20} +12°6'; acid number, 0·7; saponification number, 4·9; it dissolves in 3·5 vols. of alcohol (90%). The acetylated oil has n_D^{20} +14°16'; saponification number, 14·7. The oil from the latter is yellow. Its constants are D_{15}^{20} 0·8723; n_D^{20} +9°10'; soluble in 3 vols. of 90% alcohol; acid number, 1·05; saponification number, 9·8; saponification number after acetylation, 26·6; n_D of acetylated oil, +8°36'.

Practically no oil could be extracted from the seeds of *C. sempervirens*. The strobiles, freed from seeds, yielded 0·415% of an amber-coloured oil, D_{15}^{20} 0·8739; n_D^{20} +29°52'; soluble in 4 vols. of 90% alcohol; acid number, 1·0; saponification number, 9·8; saponification number after acetylation, 21·0; n_D of acetylated oil, +29°48'.

H. W.

Components of the Essence of Seseli bocconi. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 116—121. Compare A., 1912, i, 123).—In addition to *l*-pinene and β -phellandrene, previously recorded, this oil contains a dicyclic aldehyde, a second carbonyl compound accompanying the aldehyde, a dicyclic primary alcohol, an unsaturated secondary alcohol, and *d*- α -methylbutyric, formic and acetic acids.

Oxidation of the primary alcohol with potassium dichromate and sulphuric acid yields an aldehyde, the semicarbazons of which,



has m. p. 148—158°. This aldehyde appears to be identical with that of the essential oil mentioned above, so that the aldehyde of the oil probably has the formula $C_{10}H_{16}O$, and the alcohol the composition $C_{10}H_{18}O$.

R. V. S.

New Biochemical Syntheses of Glucosides of Alcohols. ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], 8, 109—112).—Positive results indicating the formation of β -glucosides have been obtained with the following alcohols. In all cases 100 c.c.

of acetone, containing 20 grams of water per 100 grams of acetone, and 2 grams of dextrose were used, and varying quantities of alcohol and emulsin added. The isolation and characterisation of the glucosides has not yet been effected. The alcohols used were octyl, hexadecyl, benzaldehydecyanohydrin, cyclohexanol, 2-methylcyclohexanol, α -naphthyl, borneol, morphine, also *tert*-amyl alcohol and ethylphenylglycolyl ether.

Evidence is also quoted for the synthesis of α -glycerolglucoside. The action of dried yeast on a solution containing 4 grams of salicin and 5 grams of dextrose per 100 c.c. caused an increased dextrorotation. This is considered to indicate the attachment of the alcoholic hydroxyl in salicin to dextrose in the α -position.

E. F. A.

Biochemical Synthesis of Glucosides of Multivalent Alcohols: α -Glucosides of Glycerol and Glycol. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1913, 157, 405—408).— α -Glucosidase is capable of exerting a synthesising effect on solutions of glycerol and dextrose in water, the optimum effect being obtained with solutions containing 60 grams of glycerol in 100 c.c. The product is hydrolysed on the addition of water and maceration with more of the α -glucosidase (compare Bayliss, this vol., i, 919). Mixtures of glycol and dextrose are similarly synthesised, the reaction being more rapid than with glycerol.

W. G.

Cymarin, the Active Principle of *Apocynum cannabinum* and *Apocynum androsaemifolium*. E. IMPENS (*Pflüger's Archiv*, 1913, 153, 239—275).—Finnemore (P., 1909, 25, 77) obtained as the active principle of the roots and rhizomes of *A. cannabinum*, "cynotoxin," whilst Moore (T., 1909, 95, 734) prepared from *A. androsaemifolium*, "apocynamarin." It is now shown that these plants really contain the same bitter principle, *cymarin*, which is so susceptible to the influence even of weak organic acids that the two substances mentioned above may well be decomposition products. Taub and Fickewirth have isolated it by extracting the drug with carbon tetrachloride, dissolving the extract with alcohol, precipitating resins by means of warm water, clarifying the filtrate with basic lead acetate, and, after removing the lead and concentrating under reduced pressure, extracting the residue with chloroform. The cymarin was then precipitated by light petroleum and recrystallised from methyl alcohol. It forms colourless, glistening prisms, m. p. 135—140°, C=63.6%, H=8.4%. It is not a glucoside. A series of pharmacological experiments is described which shows that it corresponds in activity with digitalis, being slightly more potent as a diuretic and slightly less so as a cardiac stimulant.

J. C. W.

Action of Alkylloxides on Hæmin and its Derivatives. I. Simplification of Hæmin by Potassium Alkoxides and a New Formation of Mesoporphyrin. HANS FISCHER and HEINRICH RÖSE (*Zeitsch. physiol. Chem.*, 1913, 87, 38—50).—On heating hæmin in an autoclave with potassium methoxide at 220° a considerable quantity of phyllopyrrole is obtained, together with a little trimethylpyrrolepropionic acid.

With potassium ethoxide a mixture of the two dimethyldiethylpyrroles is formed:



in which (I) predominates.

The reaction with alkylloxides is accordingly similar to the reduction effected by hydrogen iodide in the α -position; alkylation follows the simplification of the molecule by reduction.

The hæmin complex remains intact when it is heated with sodium methoxide at 200° . On treatment of the reaction product with hydrogen bromide in acetic acid, the iron is eliminated and meso-porphyrin obtained.

E. F. A.

The Difference between the Hæmocyanins according to their Zoological Origin. CHARLES DHÉRE (*Compt. rend.*, 1913, 157, 309—312).—The preliminary results of an investigation into the differences in composition, constitution, and properties of hæmocyanins derived from the blood of different classes of invertebrates. The specimens examined were precipitated more or less completely on dialysis, the oxyhæmocyanin from the snail being obtained in a crystalline form, whilst the others were all amorphous. The behaviour was also varied on applying the biuret test for copper by addition of aqueous sodium hydroxide. Variations were found in the colour of solutions of different samples in $N/10$ -acetic acid, but they all exhibited similar ultra-violet absorption spectra.

W. G.

Studies on Melanin. V. A. Comparison of Certain Nitrogen Ratios in Black and in White Wool from the Same Animal. ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1913, 35, 1262—1268. Compare A., 1910, i, 760; 1911, ii, 908; 1912, i, 290).—In order to determine if possible whether the chromogen utilised in the formation of melanin is part of the normal structure of keratin or whether it is secreted solely for pigment formation, the author has made comparative analyses of black and white wool from the same animal. No definite conclusion can be drawn, although the evidence seems somewhat in favour of the latter view.

The distribution of nitrogen in the two wools is very similar, with the exception that the presence of the pigment in black wool causes an excess of 3.54% in the humin nitrogen with a corresponding deficiency of 2.50% in the amino-nitrogen in the filtrate from the bases. The total nitrogen content of the white wool was 16.27%, whilst that of the black wool was 15.11%.

D. F. T.

[Carminic Acid.] OTTO DIMROTH (*Annalen*, 1913, 399, 378).—The author has received information that cochineal, contrary to his recent statement (this vol., i, 977), has been used in dyeing cotton.

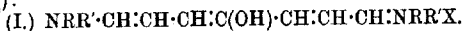
C. S.

Green Animal Colouring Matters. HANS PRZIBRAM (*Pflüger's Archiv*, 1913, 153, 385—400).—The green colouring matters in *Bacillus Rossi*, *Disippus morosus*, grasshoppers, locusts, Egyptian

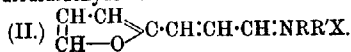
praying-crickets, the Spanish fly, the skin of frogs, *Bonellia viridis*, and the leaves of the sea-lettuce, fir, syringa, maize, and blackberry have been compared. Ethereal or sometimes alcoholic extracts of equal colour intensity were heated for some time with saturated alcoholic potassium hydroxide, treated with a few drops of concentrated sulphuric or nitric acid, and also examined in the spectroscope. Many authors have doubted that the pigment in these animals is essentially different from chlorophyll, but the present investigations confirm the author in his view that animals develop a different colouring matter. Only in the case of the plant-eating insects could there be any suspicion, from the spectroscopic examination, that a little genuine plant chlorophyll was also present in the extract. In the flesh-eating insects, even in the wing cases of the praying-cricket, there is a different pigment, "animal green." The sea-worm, *Bonellia viridis*, contains a pigment of its own, "bonellein."

The author reviews the literature on the absorption spectra of chlorophyll and animal colouring matters, and finally tabulates the following characteristics. I. Chlorophyll.—Becomes turbid and precipitates black, flocculent masses on heating with alcoholic potassium hydroxide for some time; is only slightly bleached by strong acids, and shows a strong absorption band between 544 and 537 μ . II. Animal green.—Deposits coloured masses and clarifies with alcoholic potassium hydroxide; almost bleached by fuming nitric acid; rendered turbid and brown by sulphuric acid; shows no distinct band between 544 and 537 μ , and no shadow near 630 μ . III. Bonellein.—Coloured violet or blue by strong acids; shows a number of weak bands, and a strong one between 651 and 623 μ . J. C. W.

Azomethine Dyes from β -Furylacraldehyde. WILHELM KÖNIG (*J. pr. Chem.*, 1913, [ii], 88, 193—226).—In the presence of perchloric and hydrobromic acids, β -furylacraldehyde readily reacts with primary aromatic amines and with secondary amines of the tetrahydroquinoline and dihydroindole series in alcoholic solution, yielding blue dyes, related to the furfuraldehyde dyes already described by the author (*A.*, 1906, i, 109) and having the following constitution ($X = \text{Br}$ or ClO_4):



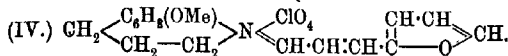
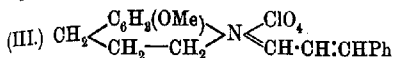
The dyes give violet-blue or greenish-blue alcoholic solutions, which rapidly lose their colour when kept. This disappearance of the blue colour is due to the removal of one of the amine residues and the formation of furfuraldehyde derivatives of the formula:



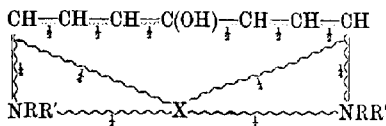
The latter compounds have been isolated in the form of their perchlorates, (i) by heating the perchlorates of the blue dyes, derived from cyclic secondary amines, in glacial acetic acid solution, and (ii) by the direct interaction of molecular amounts of the amines and β -furylacraldehyde in an alcoholic solution of perchloric acid.

That these compounds have the above constitution (II) and not the open-chain formula, $\text{NRR}'\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$, has been

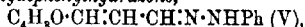
established (i) by the action of phenylhydrazine, which results in the removal of the amino-group and the formation of β -furylacraldehyde-phenylhydrazone (V below), and (ii) by the great similarity in the absorption spectra of the perchlorates of the condensation products, formed by cinnamaldehyde and β -furylacraldehyde with 6-methoxy-tetrahydroquinoline (thalline); the condensation product from cinnamaldehyde undoubtedly has the constitution represented in formula III, and hence the analogous product from β -furylacraldehyde must be represented by a similar formula (IV).



The author discusses both the mechanism of the formation of the dyes and also the relationship between their absorptive power and constitution from the point of view of Kauffmann's theory of partial valency, and, using Gebhard's method of representing the distribution of the partial valencies, assigns to the dyes the following constitution :



β -Furylacraldehydephenylhydrazone,



prepared from its components in alcoholic solution, is precipitated from the latter solution in citron-yellow needles, which are transformed by crystallisation from light petroleum into colourless crystals, m. p. 132°.

β -Furylacraldehyde condenses with *m*-nitroaniline in boiling alcoholic solution, yielding the *anil*, $\text{C}_6\text{H}_5\text{O} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$. This forms citron-yellow needles, m. p. 105°, and yields a *perchlorate*, which crystallises in orange prisms, and is converted by contact with primary or secondary aromatic amines into blue dyes.

The dyes described below were all prepared by the addition of the requisite amine (2 mols.) to a well cooled solution of β -furylacraldehyde (1 mol.) in a small quantity of alcohol, containing either hydrogen bromide (1 mol.) or perchloric acid (1 mol.). They all crystallise with H_2O .

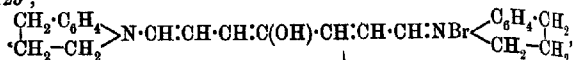
The *bromide* of the dye from the aniline (formula I, R = H, R' = Ph, X = Br) crystallises in dark bluish-green, microscopic needles, m. p. about 102°; the *perchlorate* in blue needles, m. p. 90°.

The *perchlorate* of the dye from *m*-toluidine forms blue needles, m. p. 108°; that from *p*-anisidine has m. p. about 115°.

The *bromide* of the dye from methylaniline (I, R = Me, R' = Ph) has m. p. 103°, and on treatment with aniline is converted into the

corresponding dye derived from aniline; the perchlorate forms lustrous, blue needles, m. p. 110°.

Tetrahydroquinoline yields a dye which forms a bromide, m. p. about 125°,



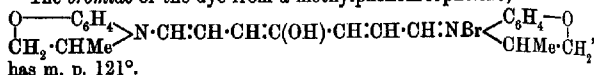
and a perchlorate, m. p. 118°.

The perchlorates of the dyes from 6-methyl- and 5-methyl-tetrahydroquinolines have m. p. 132° and 126° respectively.

The dye from 6-methoxytetrahydroquinoline forms a bromide, m. p. 129°, and a perchlorate, m. p. 121°.

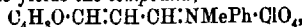
2-Methyldihydroindole yields a dye, of which the bromide has m. p. 138°, and the perchlorate, m. p. 131°.

The bromide of the dye from α -methylphenomorpholine,



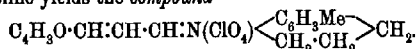
has m. p. 121°.

When heated in acetic acid solution the perchlorate of the dye from methylaniline yields the compound,



which forms citron-yellow crystals, m. p. 176°, and is transformed into the original perchlorate on treatment with methylaniline.

In a similar manner the perchlorate of the dye from 6-methyltetrahydroquinoline yields the compound



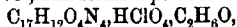
On crystallisation from glacial acetic acid this separates in long red and yellow needles, m. p. 204°, which have the same composition and cannot be separated by crystallisation from solvents; the yellow modification passes into the red form on continued heating at 140—150°.

The perchlorate of the condensation product from 6-methoxytetrahydroquinoline and β -furylacetaldehyde (formula IV), prepared by mixing the components in molecular proportions in alcoholic solution, forms red crystals, m. p. 188°, resembling chromium trioxide.

The corresponding perchlorate from cinnamaldehyde (III) forms orange crystals, m. p. 204°; the bromide crystallises in long, orange-red needles, m. p. 185°, containing $1\text{H}_2\text{O}$.

By the interaction of furfuraldehyde and *m*-nitroaniline in alcoholic solution, Schiff (A., 1880, 391) obtained a substance, which he considered to have the formula: $\text{C}_4\text{H}_5\text{O} \cdot \text{CH}(\text{OH}) \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$. The author finds, however, that the substance is not a furfuraldehyde derivative, but a pyrrole derivative of the following

constitution: $\text{CH} < \begin{array}{c} \text{CH} - \text{CH} \\ \text{N}(\text{C}_6\text{H}_4 \cdot \text{NO}_2) \end{array} > \text{C} \cdot \text{CH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$. It separates from ethyl alcohol in orange-yellow crystals, containing the solvent (1 mol.), m. p. 167—168°, and forms a perchlorate,

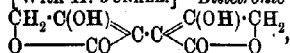


which crystallises in microscopic, brownish-red needles, m. p. 173° (decomp.).

Details of the methods employed in the spectrographic examination of the compounds described in the paper are also given. F. B.

ORGANIC CHEMISTRY.

Derivatives of Tetronic Acid. LUDWIG WOLFF (*Annalen*, 1913, 399, 309—316).—[With H. JUNKER.]—Bistetronic acid,

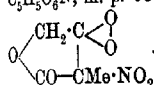


m. p. 235°, colourless, crystalline powder, is obtained by heating *ethyl dibromodiacetylsuccinate* (prepared by the bromination of ethyl diacetylsuccinate in chloroform) at 150—160°, or by treating a boiling aqueous solution of bromotetrone acid with propylidenebistetronic acid and sodium carbonate and subsequently acidifying the solution. Bistetronic acid and ferric chloride develop a blue coloration in aqueous solution and a green in alcohol. The *amide*, $\text{C}_{14}\text{H}_{11}\text{O}_5\text{N}$, m. p. 216°, crystallises in leaflets, and the *dibenzoyl* derivative, $\text{C}_{22}\text{H}_{14}\text{O}_8$, m. p. 215°, in needles.

[With W. HEROLD.]—In general, α -alkyltetrone acids are converted by nitrogen trioxide into nitroso-compounds, $\text{O} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \diagdown \quad \diagup \\ \text{CO} \quad \text{CR} \cdot \text{NO} \end{array}$ in the

absence of water, and into oximes, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{CR} \cdot \text{NOH}$, in the presence of water; in the latter case, when the alkyl group R contains more than one carbon atom, it is eliminated in the form of an aldehyde and α -oximinotetrone acid is obtained. Thus 2-ethyltetrone acid and hot aqueous sodium nitrite, in the presence of a little hydrochloric acid, yield acetaldehyde, α -oximinotetrone acid, and α -oximinobutyrylglycollic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}(\text{Et}) \cdot \text{NOH}$, m. p. 171°, colourless needles. In a similar manner, 2-benzyltetrone acid yields benzaldehyde, 2-oximinotetrone acid, and α -oximinobenzylglycollic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}(\text{NOH}) \cdot \text{CH}_2\text{Ph}$, m. p. 146°, which dissolves in concentrated nitric acid with a blue colour, and is converted into α -oximinobenzylglycollic acid by hot aqueous sodium hydroxide, and into the corresponding *amide*, $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_2$, m. p. 147°, needles, by aqueous ammonia.

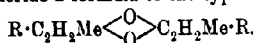
By treatment with 100% nitric acid at 0°, 2-methyltetrone acid or 2-nitroso-2-methyltetrone acid is converted into a neutral *substance*, $\text{C}_5\text{H}_5\text{O}_6\text{N}$, m. p. 68°, colourless plates, which probably has the formula



It does not react with ferric chloride or respond

to Liebermann's nitroso-reaction, exhibits powerful oxidising properties, and is decomposed by boiling water into dimethyl diketone, hydrogen cyanide, carbon dioxide, and nitric acid. In a similar manner, 2-nitroso-2-ethyltetrone acid is converted into a *substance*, $\text{C}_6\text{H}_7\text{O}_6\text{N}$, m. p. 43°, colourless needles. C. S.

Structural Formula of the Polymeride of the Anhydride of Anethole Glycol. LUIGI BALBIANO (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 93—94. Compare A., 1908, i, 901).—The author now assigns to this polymeride a formula of the type



R. V. S.

Reactions of the Formamidines. III. Synthesis of *iso*-Oxazolone, *iso*Oxazole, Cyanoacetic and Benzoylacetic Acid Derivatives. FRANK BURNETT DAINS and E. L. GRIFFIN (*J. Amer. Chem. Soc.*, 1913, 35, 959—970).—In extension of the earlier work (compare A., 1902, i, 602; A., 1909, i, 781) it is found that the methylene

group of the *isooxazolones* of the general formula $\begin{matrix} \text{CH}_2\text{CO} \\ \text{CR}=\text{N} \end{matrix} > \text{O}$, like that of phenylmethylpyrazolone is capable of reacting with the arylformamidines.

Diphenylformamidine reacts with an equimolecular quantity of phenylisooxazolone at 120°, yielding aniline and 3-phenyl-4-anilinomethylene-5-isooxazolone, $\begin{matrix} \text{O}-\text{CO} \\ \text{N:CPh} \end{matrix} > \text{C:CH-NHPh}$, yellow, rhombic

crystals, m. p. 145°; in a similar manner, di-*o*-tolylformamidine gives 3-phenyl-4-*o*-toluidinomethylene-5-isooxazolone, yellow crystals, m. p. 170°; 3-phenyl-4-*m*-toluidinomethylene-5-isooxazolone, yellow crystals, m. p. 158°; 3-phenyl-4-*p*-toluidinomethylene-5-isooxazolone, slightly red crystals, m. p. 190°; 3-phenyl-4-*o*-anisidinomethylene-5-isooxazolone, yellow needles, m. p. 138°; 3-phenyl-4-*p*-anisidinomethylene-5-isooxazolone, m. p. 168°; 3-phenyl-4-*p*-phenetidinomethylene-5-isooxazolone, m. p. 174°; 3-phenyl-4-*ψ*-cumidinomethylene-5-isooxazolone, yellow needles, m. p. 180°; 3-phenyl-4-*m*-nitroanilinomethylene-5-isooxazolone, yellow needles, m. p. 206°, and 3-phenyl-4-*p*-bromoanilinomethylene-5-isooxazolone, a pale yellow substance, m. p. 198°, are all obtainable similarly by applying the suitably substituted formamidine. The last-named product can also be obtained by the action of bromine on an acetic acid solution of phenylanilinomethyleneisooxazolone, when an intermediate red monobromo-compound, m. p. 148°, is produced, which undergoes rearrangement in solution in pyridine or alcohol with formation of the phenylbromoanilinomethyleneisooxazolone.

No derivatives could be obtained from 3-methylisooxazolone by heating with formamidines as the temperature necessary to induce interaction caused decomposition of the products. Benzylidenemethylisooxazolone, however, if heated with an equimolecular proportion of diphenylformamidine at 115—120°, yielded a mixture of benzylidene-aniline with 4-anilinomethylene-3-methyl-5-isooxazolone, pale yellow crystals, m. p. 158°, which dissolves unchanged in cold dilute alkalis, but with a warm solution of potassium hydroxide undergoes decomposition with deposition of aniline and needles of a potassium salt, decomp. 265—270°, of an unidentified substance; the above condensation product also reacts with bromine in acetic acid solution with precipitation of a yellow substance, which loses hydrogen bromide on drying, and when dissolved in alcohol or boiled with water or pyridine undergoes rearrangement into *p*-bromoanilinomethylenemethylisooxazolone, yellow needles, m. p. 204°, also obtainable from benzylidenemethylisooxazolone and di-*p*-bromodiphenylformamidine. A similar rearrangement has been previously noted (A., 1902, i, 602), the substance m. p. 148° having been since recognised as ethyl α -cyano- β -*p*-bromoanilinoacrylate, $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}:\text{H}\cdot\text{CH}:\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, and the explanation of this change appears to be expressed by the following

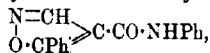
series of equations: $\text{CHR}_2\cdot\text{CH}\cdot\text{NPh} + \text{Br}_2 = \text{CHR}_2\cdot\text{CHBr}\cdot\text{NBrPh} = \text{CR}_2\cdot\text{CH}\cdot\text{NBrPh} + \text{HBr} \rightarrow \text{CR}_2\cdot\text{CH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}$, in the first stage of which the tautomeric form of the anilinoethylene derivative is involved. Diphenylformamidine also combines with bromine, giving a yellow additive product, m. p. 262° , which on treatment with potassium hydroxide solution decomposes into *p*-bromoaniline, *p*-bromofornanilide, and aniline.

That the reaction between benzylidenemethylisooxazolone and formamidines is a general one is evidenced by the following compounds which were also prepared: 4-*o*-toluidinomethylene-3-methyl-5-isooxazolone, pale red needles, m. p. 206° ; 4-*m*-toluidinomethylene-3-methyl-5-isooxazolone, brownish-white needles, m. p. 168° ; 4-*p*-toluidinomethylene-3-methyl-5-isooxazolone, yellow needles, m. p. 204° , which is decomposed by an alcoholic solution of hydrogen chloride with formation of ammonium chloride and *p*-toluidine hydrochloride, and on treatment with bromine in acetic acid solution gives a yellow additive product, m. p. $161\text{--}163^\circ$; this regenerates the original substance when acted on by alcohol or potassium hydroxide; 4-*p*-anisidinomethylene-3-methyl-5-isooxazolone, yellow needles, m. p. 190° ; 4-*p*-phenetidinomethylene-3-methyl-5-isooxazolone, yellow needles, m. p. 169° ; 4-*m*-xylylidinomethylene-3-methyl-5-isooxazolone, colourless crystals, m. p. 166° ; 4-*o*-anisidinomethylene-3-methyl-5-isooxazolone, yellow crystals, m. p. 169° .

p-Methoxybenzylidenemethylisooxazolone, deep yellow crystals, m. p. 178° , was prepared by a similar method to the corresponding benzylidene compound, namely, by the action of anisaldehyde and hydrochloric acid on the reaction mixture obtained from ethyl acetoacetate and hydroxylamine hydrochloride in aqueous alcohol containing some pyridine. It reacts with the formamidines in a similar manner to the benzylidene derivative, and on heating with di- ψ -cumylformamidine gave 4- ψ -cumidinomethylene-3-methyl-5-isooxazolone, a yellow, crystalline substance, m. p. 192° , together with anisylidene- ψ -cumidine, colourless crystals, m. p. 71° .

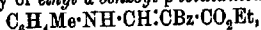
When a suspension of benzoylanilinomethyleneacetanilide,
 $\text{NPh}\cdot\text{CH}\cdot\text{CBz}\cdot\text{CO}\cdot\text{NPh}$,

in alcohol is warmed for several hours with rather more than an equimolecular proportion of hydroxylamine hydrochloride and pyridine, there is produced 5-phenylisooxazole-4-carboxyanilide,



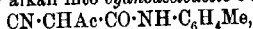
colourless needles, m. p. 135° , from the solutions of which in alkali acids precipitate benzoylcyanacetanilide, $\text{CN}\cdot\text{CHBz}\cdot\text{CO}\cdot\text{NPh}$, m. p. 203° . In a similar manner, 5-phenylisooxazole-4-carboxy-*o*-toluidide, colourless needles, m. p. 114° , can be obtained from *o*-toluidinomethylenebenzoylaceto-*o*-toluidide, and by solution in alkali and reprecipitation by acid is converted into benzoylcyanaceto-*o*-toluidide, colourless needles, m. p. 132° ; also 5-phenylisooxazole-4-carboxy-*p*-toluidide, colourless needles, m. p. 158° , was prepared, which by successive treatment with alkali and acid yielded benzoylcyanaceto-*p*-toluidide, colourless needles, m. p. 180° ; in the preparation of the

p-toluidinomethylenebenzoylaceto-*p*-toluidide required for the last synthesis, a quantity of *ethyl α-benzoyl-p-toluidinoacrylate*,



yellow flakes, m. p. 98° , was obtained. In an analogous manner, *p-anisidinomethylenebenzoylaceto-p-anisidide*, yellow crystals, m. p. 196° , obtainable by heating a mixture of ethyl benzoylacetate and di-*p*-anisylformamidine at 140° , could be converted into *5-methylisooxazole-4-carboxy-p-anisylamide*, colourless needles, m. p. 142° , which under the influence of alkali rearranges to *benzoylcynoaceto-p-anisidide*, colourless needles, m. p. 194° .

Derivatives of 5-methylisooxazole-4-carboxylic acid can be obtained by taking arylaminomethyleneacetoaceto-arylamides in place of the analogous derivatives of benzoylacetic acid in the immediately preceding general synthetic reaction, and the products under the influence of alkali readily pass into the corresponding amides of cyanoacetoacetic acid; 5-methylisooxazole-4-carboxy-*o*-toluidide, colourless needles, m. p. 112° , is converted by alkali into *cynoacetoaceto-o-toluidide*,



colourless needles, m. p. 110° ; 5-methylisooxazole-4-carboxy-*p*-toluidide, colourless needles, m. p. 140° , is converted by alkali into *cynoacetoaceto-p-toluidide*, colourless needles, m. p. 176° . 5-Methylisooxazole-4-carboxyanilide, a colourless substance, m. p. 136° , which rearranges to cyanoacetoacetanilide, is difficult to isolate on account of its considerable solubility.

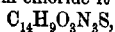
During the course of the investigation the following substances were also obtained apparently for the first time: *ethyl m-xylidinomethyleneacetoacetate*, $\text{C}_6\text{H}_4\text{Me}_2\cdot\text{NH}\cdot\text{CH}\cdot\text{CAc}\cdot\text{CO}_2\text{Et}$, colourless crystals, m. p. 122° , by heating ethyl acetoacetate with di-*m*-xylylformamidine at 120° ; *cynoaceto-m-toluidide*, colourless crystals, m. p. 138° , by heating together ethyl cyanoacetate and *m*-toluidine for several hours at 160° ; *cynoaceto-p-anisidide*, colourless crystals, m. p. 138° , by heating the two components at 160 – 170° .

D. F. T.

Oxindole and Thio-oxindole. CHARLES MARSCHALK (*J. pr. Chem.*, 1913, [ii], 88, 227–250).—A recapitulation and extension of previous work (*A.*, 1912, i, 303, 575).—Thionaphthenquinone reacts with hydrazine hydrate in boiling alcoholic solution, yielding a substance (probably a *hydrazone*), which crystallises in yellow leaflets, m. p. 128° , and when heated above its m. p. decomposes into nitrogen and thio-oxindole (2-keto-2:3-dihydro-1-thionaphthen). The latter compound is best prepared by heating *o*-thiolphenylacetic acid with phosphoric oxide in benzene solution. When prepared by this method and submitted to steam distillation, it is generally obtained in stout prisms, m. p. 44 – 45° , which on distillation under ordinary pressure are transformed into slender needles, m. p. 33 – 34° . The more fusible modification is also formed by distilling *o*-thiolphenylacetic acid alone, or heating it with acetic anhydride and distilling the product in steam. It differs from the modification of higher m. p. in giving at once a deep blue coloration with ferric chloride. Only in one instance has it been found possible to transform the modification of m. p. 33 – 34° into the

less fusible variety, a specimen of the former substance, obtained by heating *o*-thiolphenylacetic acid with phosphoric oxide in benzene solution, being converted into the modification of higher m. p. by acidifying its solution in cold aqueous sodium hydroxide.

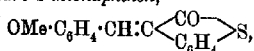
On treatment with nitrous acid, thio-oxindole yields thionaphthenquinone-3-oxime, m. p. 181° (Friedländer, A., 1908, i, 200, gives m. p. 186°). It couples with benzenediazonium chloride, yielding a substance, $C_{14}H_{10}ON_3S$, which crystallises in intensely red, lustrous needles, m. p. 159–160°, and is possibly identical with the phenylhydrazone of thionaphthenquinone (m. p. 165–166°) described by Friedländer (*loc. cit.*). With *p*-nitrobenzenediazonium chloride it forms a red *azo-dye*,



m. p. 271–272°.

The *azo-dyes* from α - and β -naphthalenediazonium chlorides crystallise in stout, brown needles, m. p. 192–193° and 154–156° respectively.

When heated with *o*-methoxybenzaldehyde in alcoholic solution in the presence of piperidine, thio-oxindole yields 2-*keto*-3-*o*-methoxybenzylidene-2:3-dihydro-1-thionaphthen,

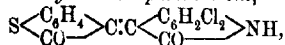


which forms yellow needles, m. p. 96–98°, and is hydrolysed by alcoholic potassium hydroxide to *o*-thiolphenyl-*o*-methoxycinnamic acid, $OMe \cdot C_6H_4 \cdot CH : C(C_6H_4 \cdot SH) \cdot CO_2H$, crystallising in stout, colourless needles, m. p. 134–136°.

It condenses with thionaphthenquinone-2-*p*-dimethylanil and acenaphthene in hot glacial acetic acid solution containing a little sulphuric acid, yielding 2:3'-bisoxythionaphthen (Friedländer, A., 1908, i, 673) and 8-oxy-6-oxythionaphthenylacenaphthene (Bezdzik and Friedländer, *loc. cit.*) respectively.

When heated with isatin in alcoholic solution, thio-oxindole forms an additive compound, $S \begin{array}{c} \diagup C_6H_4 \\ \diagdown CO \end{array} CH \cdot C(OH) \begin{array}{c} \diagup C_6H_4 \\ \diagdown CO \end{array} NH$, crystallising in colourless needles, which gradually become red at 135°, m. p. 155–160°. The additive compound gives a brown coloration with sulphuric acid, and when heated for a short time with glacial acetic acid containing a few drops of strong hydrochloric acid, is converted into 3'-indoxyl-3-thionaphthen-2'-one, $S \begin{array}{c} \diagup C_6H_4 \\ \diagdown CO \end{array} C : C \begin{array}{c} \diagup C_6H_4 \\ \diagdown CO \end{array} NH$, which crystallises in lustrous, silky, brown needles, m. p. 230°, and may also be obtained by the interaction of thio-oxindole or *o*-thiolphenylacetic acid and isatin in the presence of a mixture of glacial acetic and sulphuric acids (1:2) at the ordinary temperature.

(3')5':7'-Dichloroindoxyl-3-thionaphthen-2'-one,

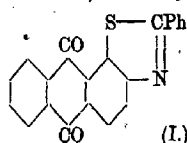


prepared by maintaining a solution of 5:7-dichloroisatin and thio-oxindole in the above acid mixture for three hours at the ordinary temperature, crystallises in dark brown needles, m. p. 330°.

The corresponding *dibromo-derivative*, from 5:7-dibromoisatin, forms brown needles, m. p. 331°.

F. B.

The Anthraquinone Series. III. Anthraquinonethiazoles. FRITZ ULLMANN and WALTHER JUNGHANS (*Annalen*, 1913, 399, 345—352).—2-Phenyl-4 : 5-(2' : 1')-anthraquinonethiazole (formula I),

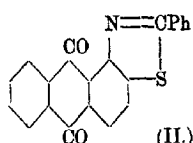


(I.)

m. p. 291° (corr.), yellowish-green needles, is obtained by boiling 2-benzylideneaminoanthraquinone with sulphur and naphthalene, or, better, by heating 1-chloro-2-aminoanthraquinone with potassium thiobenzoate and naphthalene at about 225°.

2-Phenyl-4 : 5-(1' : 2')-anthraquinonethiazole (formula II), m. p. 260° (corr.), brown needles, and 2-phenyl-

4 : 5-(2' : 3')-anthraquinonethiazole, $C_6H_4 \begin{matrix} \text{CO} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{N} \\ \text{CO} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{S} \end{matrix} \text{CPh}$, m. p.



(II.)

336—337° (corr.), faintly yellow crystals, are prepared by the latter method from 2-bromo-1-aminoanthraquinone and 3-bromo-2-aminoanthraquinone respectively. The last-mentioned thiazole does not possess dyeing properties.

1 : 3-Dibromo-2-aminoanthraquinone and potassium thiobenzoate react in boiling amyl alcohol, the initially-formed thiazole being converted into a thiazole-3 : 3'-disulphide, $C_{22}H_{20}O_4N_2S_4$, m. p. about 385°; by a similar method, 1-chloroanthraquinone is converted into the anthraquinonyl-1 : 1'-disulphide, m. p. 359°, obtained by Gattermann from anthraquinonyl-1-mercaptan.

C. S.

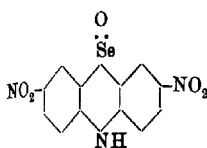
Selenodiarylamines. WILHELM CORNELIUS (*J. pr. Chem.*, 1913, [ii], 88, 395—408).—The selenium analogues of thiodiphenylamine and its derivatives are readily obtained by heating diarylamines with selenium dichloride in benzene solution (compare Weizmann and Stephen, P., 1913, 29, 196).

Selenodiphenylamine, $NH \begin{matrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{matrix} \text{Se}$, prepared from diphenylamine, crystallises in small, lustrous, yellow leaflets, m. p. 195°, which become greenish on exposure to air, owing to slight oxidation. Its constitution has been established by the formation of carbazole on distilling the substance with zinc dust or iron filings. With ferric chloride in alcoholic solution, it yields an emerald-green coloration. When heated with methyl iodide in methyl-alcoholic solution, it forms a methyl derivative, which crystallises in white needles, m. p. 138—139°, and is freed from the accompanying green oxidation product by reduction with sulphurous acid in alkaline solution. The methyl derivative resembles the parent substance in yielding various characteristic colorations on treatment with oxidising agents. It forms a yellow nitro-compound, which is converted by reduction and subsequent oxidation with ferric chloride into a red dye.

When heated with acetic anhydride, selenodiphenylamine forms an acetyl derivative, crystallising in white flakes or stout, lustrous, prismatic crystals, m. p. 176°.

On treatment with concentrated nitric acid at 0°, it yields two isomeric dinitroselenoxydiphenylamines, $C_{12}H_7O_2N_2Se$, which are readily

separated by taking advantage of the insolubility of the α -isomeride in alcohol. The α -isomeride crystallises in clusters of small, light brown needles, melts with decomposition, and dissolves in aqueous alkalis and ammonia yielding strawberry-red solutions; the white *silver* and *mercuric* salts are mentioned. On reduction and subsequent oxidation,



the α -compound gives rise to the selenium analogue of Lauth's violet, and, therefore must have the annexed constitution.

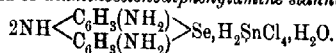
The β -isomeride forms a reddish-brown, crystalline mass, and is converted by successive reduction and oxidation into a reddish-violet *dye*. When treated with dilute nitric acid, selenodiphenylamine yields a *mononitro*-derivative, which, however, could not be separated from the accompanying dinitro-derivatives. On reducing the mixture of nitro-compounds with tin and hydrochloric acid, *aminoselenodiphenylamine*, $\text{NH} \langle \text{C}_6\text{H}_4 \rangle \text{Se}$, separates in the form of its *stannichloride*.

This crystallises in lustrous needles, and, on treatment with zinc and hydrochloric acid, yields the *zincichloride*, crystallising in small, broad, transparent needles. The free base is liberated from the latter compound by aqueous sodium hydroxide and crystallises in small, white, pearly, lustrous leaflets; the *hydrochloride* is precipitated in white needles by passing hydrogen chloride into a benzene solution of the base; the *acetyl* derivative has m. p. above 330° (decomp.).

Oxidation of the hydrochloride or zincichloride by means of ferric chloride in aqueous solution results in the formation of a dye, which is precipitated by the addition of sodium and zinc chlorides in the

form of its *zincichloride*, $2 \begin{array}{c} \text{N}-\text{C}_6\text{H}_4 \\ | \\ \text{NH}-\text{C}_6\text{H}_4 \end{array} \text{Se}, \text{H}_2\text{ZnCl}_4$. This crystallises in very slender, bronze needles, dyes silk light blue to bluish-violet, and, on the addition of alkalis to its hot alcoholic solution, yields the free base, which forms a crystalline red powder, and is converted by hydrogen chloride in ether solution into the *hydrochloride*.

α -Dinitroselenoxydiphenylamine is reduced by stannous chloride and hydrochloric acid to *diaminoselenodiphenylamine stannichloride*,



This crystallises in slender, lustrous, yellowish-brown needles, and is converted by the addition of zinc to its aqueous solution into the *zincichloride*, which is oxidised by ferric chloride to *selenonine*, the selenium analogue of Lauth's violet. The latter compound separates

in the form of its *zincichloride*, $2 \begin{array}{c} \text{N}-\text{C}_6\text{H}_3(\text{NH}_2) \\ | \\ \text{NH}-\text{C}_6\text{H}_3 \end{array} \text{Se}, \text{H}_2\text{ZnCl}_4$, in very slender, felted, reddish-brown needles, having a bronze lustre. The dye base, obtained from the zincichloride by the action of aqueous sodium hydroxide, crystallises in small bronze needles and forms a *hydrochloride*, which crystallises in long, slender, felted needles, having a bronzy-green lustre, and dyes silk turquoise-blue.

The selenium analogue of methylene-blue has been prepared by the action of hydrogen selenide on *p*-nitrosodimethylaniline and subsequent oxidation of the resulting compound with ferric chloride in hydrochloric acid solution.

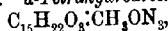
Selenophenyl-β-naphthylamine, $\text{NH} \langle \text{C}_6\text{H}_4 \rangle \text{Se}$, prepared by heating phenyl-β-naphthylamine with selenium dichloride in benzene solution, crystallises in small, yellow needles, m. p. 176°, and gives a greenish-blue coloration with sulphuric acid.

Seleno-α-dinaphthylamine, $\text{NH} \langle \text{C}_{10}\text{H}_8 \rangle \text{Se}$, from α-dinaphthylamine, forms small, yellow needles, m. p. 176–177°.

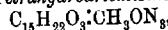
Seleno-β-dinaphthylamine crystallises from benzene in slender, felted, yellowish-green needles, from nitrobenzene in long, pointed prisms, m. p. 245°, and from alcohol in tabular crystals. On treatment with nitric acid in acetic acid solution, it yields a yellow nitro-compound.

Seleno-p-ditolylamine crystallises in yellow, lustrous, broad scales, m. p. 240°. F. B.

New Derivatives of Artemisin and of Santonin. II. ENRICO RIMINI and TEMISTOCLE JONA (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 28–32. Compare this vol., i, 748).—When artemisin is reduced with hydrogen in presence of palladium-black, α-tetrahydroartemisin, $\text{C}_{15}\text{H}_{22}\text{O}_3$, is obtained. It crystallises in plates, m. p. 193–193°, $[\alpha]_D^{25} + 49.60^\circ$ (in 2.671% alcoholic solution). From the mother-liquor a second hydro-derivative, β-tetrahydroartemisin, $\text{C}_{15}\text{H}_{22}\text{O}_3$, m. p. 165–167°, can be obtained. This substance has $[\alpha]_D^{25} + 65.15^\circ$ (in 2.670% alcoholic solution). Both tetrahydroartemisin are stable towards Baeyer's reagent. α-Tetrahydroartemisinsemicarbazone,

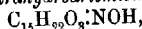


decomposes at 245°. β-Tetrahydroartemisinsemicarbazone,

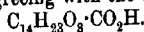


decomposes at 257–258°. α-Tetrahydroartemisinnoxime, $\text{C}_{15}\text{H}_{22}\text{O}_3 \cdot \text{NOH}$,

decomposes at 248°. β-Tetrahydroartemisinnoxime,



decomposes at 242°. Artemisinnoxime yields α-tetrahydroartemisin when hydrogenated in presence of palladium-black. When α-tetrahydroartemisin is dissolved in sodium hydroxide and the solution acidified with sulphuric acid at a low temperature, α-tetrahydroartemisinic acid can be extracted with chloroform; it softens and loses water at 55°, decomposing at 118°. Its sodium salt crystallises in needles. β-Tetrahydroartemisinic acid is similarly prepared, and is much more stable. It forms needles, m. p. 218–220° (decomp.), and on titration with alkali gives figures agreeing with the composition



R. V. S.

Action of the Halogens on Artemisin. ENRICO RIMINI and TEMISTOCLE JONA (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 71–74. Compare preceding abstract).—When a solution of artemisin in glacial acetic acid is treated with a solution of hydrogen bromide and bromine in the same solvent, artemisin dibromide hydrobromide, $\text{C}_{30}\text{H}_{57}\text{O}_8 \cdot \text{Br}_2$, is

obtained. This unstable oxonium compound, which readily loses bromine, forms lustrous, red crystals, which decompose at 94° . Under slightly different experimental conditions, the compound described is accompanied by *monobromoartemisin*, $C_{15}H_{17}O_4Br$, a stable, yellow substance which becomes red at about 70° and decomposes at 95° .

Artemisin di-iodide hydriodide, $C_{30}H_{37}O_8I_3$, similarly prepared, is a brown, crystalline substance, m. p. $118-119^{\circ}$ (decomp.).

By the action of chlorine on a chloroform solution of artemisin at 15° , a *chloroartemisin*, $C_{15}H_{15}O_3Cl_3$, is obtained, but the preparation is uncertain; the substance crystallises in needles, which decompose at 212° . When the chlorination is effected at 20° , a crystalline *chloroartemisin*, $C_{15}H_{20}O_4Cl_2$, is obtained; it decomposes at 133° .

R. V. S.

Identity of Lycorine and Narcissine. YASUHIKO ASAHINA and Y. SUGII (*Arch. Pharm.*, 1913, 251, 357-360).—The authors have examined the base lycorine, which together with a second base sekisanine was isolated by Morishima (A., 1899, i, 93) from the bulbs of *Lycoris radiata*. They are of opinion that lycorine, $C_{16}H_{17}O_4N$, m. p. 275° (decomp.), darkening at about 240° , $[\alpha]_D^{25} = 123.7^{\circ}$ in alcohol and pyridine (*hydrochloride*, colourless needles, m. p. 217° ; *picrate*, m. p. $195-202^{\circ}$ [decomp.], yellow leaflets), is identical with the alkaloid narcissine, $C_{16}H_{17}O_4N$, m. p. $266-267^{\circ}$, $[\alpha]_D = 95.8^{\circ}$, colourless prisms (*hydrochloride*, m. p. $198-199^{\circ}$, colourless needles; *picrate*, m. p. $196-199^{\circ}$, yellow leaflets), obtained by Ewins (T., 1910, 97, 2406) from the bulbs of *Narcissus pseudonarcissus*.

C. S.

Formula of apoMorphine Hydrochloride. VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 121-125).—Estimations of the water of crystallisation in *apomorphine hydrochloride* from various sources all indicate $\frac{3}{2}H_2O$. The amount of chlorine in the salt is that required by the formula $C_{17}H_{17}O_3N.HCl.\frac{3}{2}H_2O$, and the elementary analysis of *apomorphine* gives the composition $C_{17}H_{17}O_3N$. *Dibenzoyl-apomorphine* has, in freezing benzene, the composition required by the formula $C_{17}H_{15}N(OBz)_2$.

R. V. S.

Preparation of Hydrogenised Alkaloids of the Morphine Group. HERMANN OLDENBERG and BABETTE OLDENBERG (D.R.P. 260233).—Alkaloids of the morphine group are readily hydrogenised by the action of hydrogen in the presence of colloidal palladium, or a metal of the platinum group. *Hydromorphine*, $C_{17}H_{21}O_3N.H_2O$, fine needles, m. p. $155-157^{\circ}$, is obtained when morphine hydrochloride (10 parts) in 250 parts of water is shaken with a mixture of colloidal palladium (1 part) in 10 parts of water which has been saturated with hydrogen; the *hydrochloride* forms microscopic prisms; the *sulphate* is less readily obtained in crystalline form; it gives the colour reactions of Fröhde, Husemann, and Marquis.

Hydrocodeine, rhombic crystals, m. p. $62-63^{\circ}$, has also 1 mol. water of crystallisation and gives Fröhde's and Hesse's colour reactions.

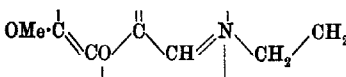
Tetrahydrothebaine, $C_{16}H_{23}O_3N$, is prepared from thebaine and responds to Fröhde's and Erdmann's reagents; the *hydrochloride* forms

prisms; the *hydrogen tartrate* is obtained by the reduction of thebaine hydrogen tartrate.

The therapeutic action of these compounds is also discussed.

F. M. G. M

Berberine. II. Berberrubine. GEORG FRERICHES and P. STORPEL (*Arch. Pharm.*, 1913, 251, 321—339).—Berberrubine is best obtained by heating well dried berberine chloride at about 190° in a slow current of carbon dioxide. There can be little doubt that anhy-



drous berberrubine contains the annexed group. Since it is readily converted into berberine iodide by treatment with methyl iodide,

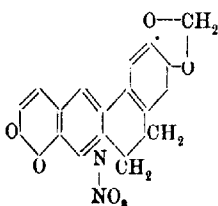
other alkyl haloids may be expected to produce homologous berberines. Thus a large excess of ethyl iodide on the water-bath converts berberrubine into *ethylberberrubine iodide* (*homoberberine iodide*), $C_{21}H_{20}O_4NI$, yellow or yellowish-brown needles, which reacts with boiling alcoholic $N/2$ -potassium hydroxide and acetone to form *ethylberberrubineacetone*, $C_{24}H_{25}O_5N$, m. p. 159°, from which the salts of ethylberberrubine are obtained by heating with dilute acids; the *chloride*, $C_{21}H_{20}O_4NCl \cdot 2H_2O$, is described.

By boiling with dilute acetic and sulphuric acids and zinc and a little platinum, ethylberberrubine chloride is reduced and yields, after basification with aqueous ammonia, *ethyltetrahydroberberrubine*, $C_{21}H_{25}O_4N$, m. p. 129°, faintly yellow crystals, which resembles tetrahydroberberine throughout.

Berberrubine reacts additively, not only with alkyl haloids, but also with other organic halogen compounds. Ethyl bromoacetate and alcohol on the water-bath convert it into the *bromide of ethyl berberrubineacetate*, $C_{23}H_{23}O_5NBr$, yellow crystals, which is converted by digestion with silver oxide and hot water into *berberrubineacetic acid*, $C_{21}H_{17}O_5N \cdot 5H_2O$; a hot aqueous solution of the latter is converted into the *hydrochloride*, $C_{21}H_{17}O_5N \cdot HCl \cdot 2H_2O$, yellow crystals, by *N*-hydrochloric acid.

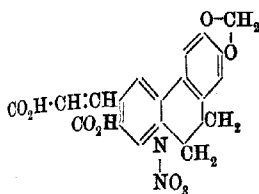
In a similar manner, berberrubine and ethyl α -bromopropionate yield the *bromide of ethyl berberrubinepropionate*, $C_{24}H_{24}O_5NBr$, yellow needles, from which *berberrubinepropionic acid*, $C_{22}H_{19}O_5N \cdot 2H_2O$, yellow needles, is obtained; the *hydrochloride* of the latter also crystallises in yellow needles. Berberrubine does not react with ethyl β -iodopropionate.

Berberrubine, unlike berberine, is attacked by oxidising agents



most readily in its methoxylated benzene nucleus. By treatment with hot 25% nitric acid it yields two crystalline substances, berberrubinone and berberrubinic acid, both of which are obtained in the form of nitrates. *Berberrubinone nitrate* (annexed formula) forms dark green, almost black, crystals, which are deep red by transmitted light, is converted into a *sulphate* (or mixture of normal and hydrogen sulphates), dark green crystals, by hot dilute sulphuric acid,

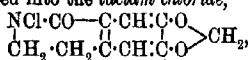
and by treatment with boiling dilute sulphuric acid and 30% sodium hydrogen sulphite is reduced to the sulphate of the corresponding quinol, *berberrubinal sulphate*, a yellow substance. From the hot solution of the latter, saturated sodium hydrogen carbonate liberates *berberrubinal*, $C_{18}H_{13}O_4N \cdot 3H_2O$, an amorphous, dark red powder.



Anhydrous *berberrubinal* is a phenyl betaine, and is therefore a completely demethylated berberine; it is not identical with Perkin's berberoline, which has the same composition.

Berberrubinic acid nitrate (annexed formula) and the corresponding *chloride*, $C_{18}H_{14}O_4NCl$, form golden-yellow crystals, and are decomposed by water with the formation of *berberrubinic acid*, an amorphous, yellow substance, which is probably a betaine; it has not been obtained entirely free from the nitrate or chloride.

A hot aqueous solution of *berberrubine* is converted by sodium hypochlorite into *chloroberberrubine*, $C_{19}H_{15}O_4NCl$, reddish-brown needles, which forms a *chloride*, $C_{19}H_{15}O_4NCl \cdot 3H_2O$, orange-yellow crystals. *Chloroberberrubine* certainly contains the chlorine atom in the methoxylated benzene nucleus (probably in the meta-position to the methoxy-group), because by the prolonged action of sodium hypochlorite it is converted into the *lactam chloride*,



m. p. 114° , colourless needles, of ω -aminoethylpiperonylcarboxylic acid; the lactam-chloride, which can also be obtained by the action of sodium hypochlorite on berberine chloride or bromoberberrubine in hot aqueous solution, is converted into Perkin's lactam, m. p. 181° , by treatment with hot aqueous sodium sulphite.

Chloroberberrubine is reduced to *chlorotetrahydroberberrubine*, $C_{19}H_{17}O_4NCl$, m. p. 142° , colourless crystals (*hydrochloride*, white, crystalline powder), by zinc and platinum and hot dilute acetic and sulphuric acids, and reacts with methyl iodide at 100° to form *chloroberberine iodide*, $C_{20}H_{17}O_4NClI$; the latter, which resembles berberine iodide in its behaviour, reacts with alcoholic *N/2*-potassium hydroxide and acetone to form *chloroberberine acetone*, $C_{23}H_{22}O_5NCl$, m. p. 171° , yellow crystals. The following substances are obtained by methods similar to the preceding: *bromoberberrubine*, $C_{19}H_{17}O_4NBr$, reddish-brown needles, and its *chloride*, $C_{19}H_{15}O_4NClBr \cdot 3H_2O$, yellow crystals; *bromotetrahydroberberrubine*, $C_{19}H_{19}O_4NBr$, m. p. 145° , colourless crystals; *bromoberberine iodide*, $C_{20}H_{19}O_4NBrI$, golden-yellow leaflets, and *bromoberberine acetone*, $C_{23}H_{22}O_5NBr$, m. p. 153° , yellow crystals.

C. S.

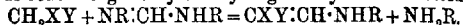
Preparation of Hydrastinine from Berberine. EMMANUEL MERCK (D.R.P. 259873. Compare Voss, A., 1910, i, 415; Freund, A., 1912, i, 383, 487).—Phenyltetrahydroberberine (m. p. 222°) when digested with methyl iodide furnishes a *methiodide*, m. p. 243° .

Phenyldihydroberberine on electrolytic reduction gives rise to two

stereoisomeric phenyltetrahydroberberines with m. p.'s 222° and $202-204^{\circ}$; these can be separated by fractional crystallisation of their sulphates; the *methiodide* of the isomeride (m. p. $202-204^{\circ}$) has m. p. 247° .

When either of the foregoing phenyltetrahydroberberines is digested with silver chloride, and subsequently reduced with sodium amalgam, it yields a *base*, $C_{27}H_{29}O_4N$, m. p. $112-113^{\circ}$ (the *hydriodide* has m. p. 218°), which on oxidation gives rise to hydrastinine. F. M. G. M.

Reactions of the Formamidines. IV. FRANK BURNETT DAINS, O. O. MALLEIS, and J. T. MEYERS (*J. Amer. Chem. Soc.*, 1913, 35, 970-976. Compare this vol., i, 1086).—The previous investigations have indicated that the general reaction of formamidines with compounds containing methylene hydrogen may be formulated:



If Y is a carbethoxy-group the amine produced can react with it to give an amide and an alcohol. The occurrence of the second reaction is more marked the higher the temperature.

p-Aminophenylbenzyl ether (hydrochloride, m. p. $222-223^{\circ}$; *benzoyl* derivative, m. p. $226-227^{\circ}$; *benzylidene* derivative, colourless leaflets, m. p. 118° ; *anisylidene* derivative, m. p. 150°) when warmed with ethyl orthoformate readily enters into reaction, producing *di-p-benzoyloxydiphenylformamidine*, $C_6H_5O \cdot C_6H_4N:CH \cdot NH \cdot C_6H_4OC_6H_5$, colourless crystals, m. p. 153° ; *hydrochloride*, m. p. 261° ; *picrate*, m. p. 209° . When heated with ethyl cyanoacetate at $120-130^{\circ}$, the formamidine reacts, producing aminophenylbenzyl ether and *ethyl α -cyano- β -benzoyloxyanilinoacrylate*, $CH_2Ph \cdot O \cdot C_6H_4 \cdot NH \cdot CH:C(CN) \cdot CO_2Et$, brown crystals, m. p. 120° . The formamidine reacts in the usual manner with ethyl malonate, giving *ethyl p-benzoyloxyanilinomethylenemalonate-p-benzoyloxyanilide*, colourless crystals, m. p. 131° , as with ethyl malonate the molecule of amine produced in the first stage of the reaction is always found to enter into amide formation. Ethyl acetoacetate with the formamidine yields products of both the first and second stages of the reaction, giving *ethyl p-benzoyloxyanilinomethylenecoacetate*, $CH_2Ph \cdot O \cdot C_6H_4 \cdot NH \cdot CH:CAc \cdot CO_2Et$, a pale yellow substance, m. p. 95° , together with *p-benzoyloxyanilinomethylenecoacetate-p-benzoyloxyanilide*, fine, yellow needles, m. p. 164° .

As was to be expected from experiments with other formamidines, phenylmethylpyrazolone readily reacts with *di-p-benzoyloxydiphenylformamidine*, giving *1-phenyl-4-p-benzoyloxyanilinomethylene-3-methyl-5-pyrazolone*, red needles, m. p. 181° .

When ethyl orthoformate is heated with *p*-aminodimethylamine at 125° for two hours, *di-p-dimethylaminodiphenylformamidine*, m. p. 157° , is obtained, which gives a yellow *monohydrochloride*, m. p. 233° , a *dihydrochloride* and a colourless *trihydrochloride*, m. p. 193° ; *picrate*, m. p. 172° . The formamidine reacts with ethyl malonate, yielding *ethyl p-dimethylaminoanilinomethylenemalonate-dimethylaminoanilide*, $NMe_2 \cdot C_6H_4 \cdot NH \cdot CH:C(CO_2Et) \cdot CO \cdot NH \cdot C_6H_4 \cdot NMe_2$, m. p. 142° , and with ethyl cyanoacetate giving *ethyl α -cyano- β -p-dimethylaminoanilinoacrylate*, $NMe_2 \cdot C_6H_4 \cdot NH \cdot CH:C(CN) \cdot CO_2Et$, colourless needles, m. p. 134° . When heated with ethyl acetoacetate the amidine produced phenylene-

dimethyldiamine and *p*-dimethylaminoanilinomethyleneacetoaceto-*p*-dinethylaminocanilide, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH} : \text{C}(\text{Ac}) \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, m. p. 178°, together with a little ethyl dimethylaminoanilinomethyleneacetoacetate, m. p. 88°.

Di-p-iododiphenylformamidine, $\text{C}_6\text{H}_4\text{I} \cdot \text{N} : \text{CH} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{I}$, colourless needles, m. p. 175°, is easily obtained by the combination of *p*-iodoaniline and ethyl orthoformate at water-bath temperature; *hydrochloride*, m. p. 249°; *picrate*, dark yellow crystals, m. p. 226°. With ethyl cyanoacetate at 125°, it produces ethyl α -cyano- β -*p*-iodoanilinoacrylate, brown needles, m. p. 154°, whilst with ethyl malonate ethyl *p*-iodoanilinomethylenemalonate-*p*-iodoanilide,

$\text{C}_6\text{H}_4\text{I} \cdot \text{NH} \cdot \text{CH} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{I}$, colourless crystals, m. p. 176°, is obtained. With ethyl acetoacetate the products are iodoaniline, ethyl *p*-iodoanilinomethyleneacetoacetate, $\text{C}_6\text{H}_4\text{I} \cdot \text{NH} \cdot \text{CH} : \text{C}(\text{Ac}) \cdot \text{CO}_2\text{Et}$, colourless crystals, m. p. 96°, and *p*-iodoanilinomethyleneacetoaceto-*p*-iodoanilide, m. p. 184°. The formamidine also reacts with acetylacetone, producing *p*-iodoanilinomethyleneacetylacetone, $\text{C}_6\text{H}_4\text{I} \cdot \text{CH} : \text{CH} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{I}$, pale yellow needles, m. p. 180°, whilst with benzylidenemethylisooxazolone at 140°, 3-methyl-4-*p*-iodoanilinomethylene-5-isooxazolone, $\begin{matrix} \text{N} \cdot \text{CMe}_2 \\ | \\ \text{O} - \text{CO} \end{matrix} > \text{C} : \text{CH} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{I}$, yellow crystals, m. p. 208°, is obtained. The benzylidene derivative, m. p. 85°, and anisylidene derivative, colourless needles, m. p. 151°, of *p*-iodoaniline were also prepared.

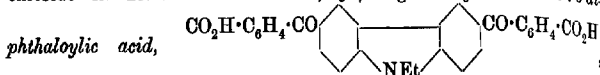
5-Iodo-*o*-toluidine (acetyl derivative, m. p. 176°, reacts quantitatively with bromine in chloroform solution producing 5-bromoaceto-*o*-toluidine, m. p. 158—159°; *benzylidene* derivative, colourless needles, m. p. 55°) also reacts with ethyl orthoformate, giving *di*-5-iododi-*o*-tolylformamidine, $\text{C}_6\text{H}_3\text{MeI} \cdot \text{N} : \text{CH} \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{MeI}$, needles, m. p. 169°; *hydrochloride*, m. p. 254°. This formamidine shows the usual behaviour towards compounds containing the methylene group, for example, with ethyl acetoacetate it forms ethyl 5-iodo-*o*-toluidinomethyleneacetoacetate, m. p. 137—138°, and 5-iodo-*o*-toluidinomethyleneacetoaceto-5-iodo-*o*-toluidide, silky needles, m. p. 238°. With ethyl cyanoacetate and malonate the reaction products are ethyl 5-iodo- α -cyano-*o*-toluidinoacrylate, m. p. 207°, and ethyl 5-iodo-*o*-toluidinomethylenemalonate-5-iodo-*o*-toluidide, m. p. 201°. At 120° with benzylidenemethylisooxazolone the formamidine gives rise to 3-methyl-4-iodotoluidinomethylene-5-isooxazolone, needles, m. p. 209°.

D. F. T.

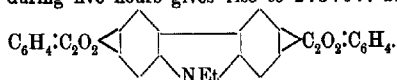
Preparation of Carbazolemonosulphonic Acids and their 9-Alkyl Derivatives. LEOPOLD CASSELLA & Co. (D.R.P. 260898. Compare this vol., i, 516).—When carbazole (17 parts) is dissolved in 10—15 parts of hot nitrobenzene and cooled to 0° (when part of the carbazole separates), treated with chlorosulphonic acid (12 parts), and the temperature subsequently allowed to rise to 20°, it furnishes carbazolesulphonic acid, which is isolated in the form of its sodium salt, colourless, glistening leaflets; the barium salt, glistening scales, is more sparingly soluble. This compound condenses with *p*-nitrosophenol in concentrated sulphuric acid solution to furnish soluble blue dyes containing sulphur.

9-Ethylcarbazolesulphonic acid can also be prepared in quantitative yield by this method. F. M. G. M.

[Preparation of 9-Ethylcarbazole-3:6-diphthaloylic Acid.] LEOPOLD CASSELLA & Co. (D.R.-P. 261495. Compare A., 1911, i, 567).—9-Ethylcarbazole reacts with phthalic anhydride and aluminium chloride in nitrobenzene solution, yielding 9-ethylcarbazole-3:6-di-



and this when heated with concentrated sulphuric acid at 100–105° during five hours gives rise to 2:3:6:7-diphthaloyl-9-ethylcarbazole,



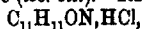
F. M. G. M.

Catalytic Decomposition of Acetonylacetonophenylhydrazone. ALEXANDER E. ARBUZOV and N. E. CHRUCKI (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 699).—Catalytic decomposition of acetonylacetonophenylhydrazone at 180–190° in presence of cuprous chloride yields ammonia, dimethylaminophenylpyrrole, benzene and aniline, the last two products probably arising from the decomposition of a little admixed phenylhydrazine. T. H. P.

Catalytic Decomposition of Methyl Propyl Ketonephenylhydrazone. ALEXANDER E. ARBUZOV and A. P. FRIAU (J. Russ. Phys. Chem. Soc., 1913, 45, 694–696).—Catalytic decomposition of methyl propyl ketonephenylhydrazone at 185–210° in presence of cuprous chloride yields, as principal product, propylindole, $\text{C}_{11}\text{H}_{13}\text{N}$, which is an almost odourless, pale yellow liquid, b. p. 155–156°/9 mm., and forms a picrate, $\text{C}_{17}\text{H}_{18}\text{O}_4\text{N}_4$, m. p. 148–149°. Small proportions of secondary gaseous and liquid products also result from the decomposition. T. H. P.

Catalytic Decomposition of Dipropyl Ketonephenylhydrazone. ALEXANDER E. ARBUZOV and R. E. VAGNER (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 697–699).—Catalytic decomposition of dipropyl ketonephenylhydrazone at 175–235° in presence of cuprous chloride yields principally 3-ethyl-2-propylindole, $\text{C}_{13}\text{H}_{17}\text{N}$, which crystallises in unstable, colourless plates, m. p. 45·5°, and forms a picrate, $\text{C}_{19}\text{H}_{21}\text{N}_4\text{O}_4$, m. p. 117·5°. Other products, including aniline, are formed in small proportions. T. H. P.

Syntheses in the Indole Group. V. Syntheses of *N*- and *C*-Substituted Derivatives of Scatole and Methylketole. BERNARDO ODDO (*Gazzetta*, 1913, 43, ii, 190–211. Compare A., 1912, i, 649; this vol., i, 755).—3-Acetyl-2-methylindole can be obtained in 86% yield by the action of acetyl chloride on the magnesium derivative of 2-methylindole (*loc. cit.*). Its hydrochloride,

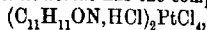


was also prepared. The *aurichloride*, $C_{11}H_{11}ON, HCl, AuCl_3$, becomes brown at about 135° , melting at 158° (decomp.). The *platinichloride*, $(C_{11}H_{11}ON, HCl)_2PtCl_4$, blackens above 170° , melting at 195° (decomp.). The hydrochloric acid solution of the ketone gives precipitates with phosphotungstic acid, potassium cadmium iodide, potassium bismuth iodide, and potassium dichromate.

1. *Acetylscatole*, $C_6H_4 \begin{matrix} \text{CMe} \\ \diagup \quad \diagdown \\ \text{CH} \end{matrix} \text{N} \text{Ac}$, is obtained by the action of acetyl

chloride on the magnesium derivative of scatole, a low temperature being maintained with ice. It forms colourless needles, m. p. 68° , and has about the normal molecular weight in freezing benzene. Its constitution is shown by its yielding scatole when treated with alcoholic potassium hydroxide, and by the fact that it gives no precipitate with silver nitrate. In the preparation of 1-acetylscatole, a substance crystallising in needles of m. p. 146° is also obtained.

2. *Acetylscatole* is obtained when the above reaction is effected at the temperature of the water-bath. Its *hydrochloride* has the composition $(C_{11}H_{11}ON)_2, HCl$, and its solution gives precipitates with phosphotungstic acid, potassium bismuth iodide, potassium dichromate, and gold chloride. The *platinichloride* has the composition



The action of propionyl chloride on the magnesium derivative of scatole yields both propionylmethylindoles, which can be separated by distillation with steam. 1-*Propionylscatole*, $C_{12}H_{13}ON$, has m. p. 45° . 2-*Propionylscatole*, $C_{12}H_{13}ON$, has m. p. 161° , and when fused with potassium hydroxide yields indole-3-carboxylic acid. 3-*Propionyl-2-methylindole*, $C_{12}H_{13}ON$, is obtained from propionyl chloride and the magnesium derivative of methylketole; it forms colourless crystals, m. p. 194° , and has about half the calculated molecular weight in freezing phenylhydrazine (*K* for phenylhydrazine is 58.59). Oxidation of the substance with potassium permanganate yields acetyl-*o*-amino-benzoic acid.

3. *Butyryl-2-methylindole*, $C_{13}H_{15}ON$, is prepared by the action of butyryl chloride on the magnesium derivative of methylketole; it is a white, crystalline substance, m. p. $157\text{--}158^\circ$, and tends to become yellow when exposed to the air.

3-Benzoyl-2-methylindole, $C_{16}H_{13}ON$ (from benzoyl chloride and the magnesium derivative of methylketole), forms colourless needles, m. p. 181° . When the reaction is effected at a low temperature, traces of a substance of m. p. 81° are produced, which is probably the 1-derivative.

R. V. S.

Condensation of Aldehydes with *N*-Mono-substituted *p*-Diamines. RICHARD SCHLÖGL (*J. pr. Chem.*, 1913, [ii], 88, 251—256).—An account of the preparation of a number of anils by the condensation of acetyl-*p*-phenylenediamine, *p*-amino-oxanilic acid, and *p*-aminophenylglycine with aromatic aldehydes.

The *salicylidene*, *cinnamylidene* (m. p. 120°), 3:4-dihydroxybenzylidene, *vanillidene*, and *furfurylidene* (m. p. 135°) derivatives of *p*-amino-

phenylglycine are prepared by warming the glycine with an alcoholic solution of the corresponding aldehyde.

The *benzylidene* derivative of *p*-aminophenyloxamic acid is obtained in the form of its *hydrochloride*, $C_{15}H_{13}O_3N_2Cl$, m. p. 180° , by heating an alcoholic suspension of the oxamic acid with benzaldehyde and hydrochloric acid.

The following compounds were prepared in a similar manner: the *hydrochlorides* of the *vanillidene* (m. p. 170°), *cinnamylidene* (m. p. 125°), and *furfurylidene* (m. p. 130°) derivatives of *p*-aminophenyl-oxamic acid, and the *hydrochlorides* of the *benzylidene* (m. p. 165°), *vanillidene* (m. p. 208°), and *cinnamylidene* (m. p. 195°) derivatives of acetyl-*p*-phenylenediamine.

The condensation product from acetaldehyde and *p*-aminophenylglycine forms a dark brown powder (decomp. 280°), insoluble in the ordinary solvents; attempts to effect a condensation of acetyl-*p*-phenylenediamine and *p*-aminophenylglycine with formaldehyde and acetaldehyde were unsuccessful.

All the derivatives mentioned above are readily resolved by boiling with water or alkali hydroxides into their components, and on account of the presence of the azomethine group, are coloured, those of *p*-aminophenylglycine being red.

F. B.

Hydrazones. LUIGI VECCHIOTTI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 75—76).—Many nitrohydrazones exist in red and in yellow modifications. The present paper gives a list of these compounds and the forms observed in each instance.

R. V. S.

Extractives of Muscle. XIV. Carnosine and Carnosine Nitrate. WLADIMIR GULEWITSCH (*Zeitsch. physiol. Chem.*, 1913, 87, 1—11. Compare A., 1900, i, 516; 1905, i, 726; 1906, i, 627; 1907, i, 264, 436).—The purification of carnosine nitrate and carnosine is described. The nitrate crystallises in large, stellate aggregates of needles, m. p. 219° (decomp.), $[\alpha]_D + 23.3^\circ$ in 5% solution. The rotatory power increases slightly on dilution; it falls to about half its value in presence of nitric acid.

Carnosine crystallises in large, colourless needles, which unite to rosettes and cauliflower-like aggregates, m. p. $246—250^\circ$ (decomp.). It has an insipid taste, and is strongly alkaline. It has $[\alpha]_D + 21^\circ$, independently of the concentration. No racemisation takes place in preparing it from the nitrate.

E. F. A.

Preparation of Chloro- and Bromo-substitution Products of Indophenols and Indophenolic Substances or their Leuco-derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 260328 and 260329).—The action of *p*-nitrosophenol on carbazoles has previously been studied (A., 1906, i, 890; 1911, i, 1025), and halogen derivatives of these compounds have now been prepared.

When 4-dimethylamino-4'-hydroxydiphenylamine (230 parts) dissolved in concentrated hydrochloric acid (1700 parts) is treated at $10—15^\circ$ with 150 parts of chlorine, it furnishes a *dichloro-4-dimethylamino-4'-hydroxydiphenylamine hydrochloride* in quantitative yield

which on oxidation gives rise to the corresponding *indophenol*. *Compounds* obtained by the action of chlorine on an *o*-dichlorobenzene solution of the following substances, and their oxidation products are described: from *p*-nitrosophenol with carbazole and the leuco-compound of the same; from *p*-nitrosophenol with *N*-methyl- or *N*-ethyl-carbazole and their leuco-compounds.

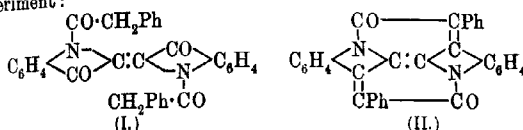
II. describes the preparation of the corresponding bromo-derivatives; in this case the reaction is carried out in *o*-dichlorobenzene solution.

F. M. G. M.

Constitution of Anilopyrine. LINO METELLO ZAMPOLLI (*Boll. chim. farm.*, 1913, 52, 502—504).—Polemical. A reply to Comanducci (this vol., i, 903).

R. V. S.

Preparation of Red Condensation Products from Indigotin, its Homologues, and Substitution Products. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 260243. Compare this vol., i, 763).—The action of phenylacetyl chloride on indigotin yields the red, crystalline compounds I or II, according to the conditions of the experiment:



Analogous compounds prepared from tetrabromoindigotin are also described, which are of a somewhat bluer shade.

F. M. G. M.

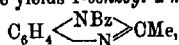
Benzoylation of Benziminazoles. LUDWIG WOLFF (*Annalen*, 1913, 399, 297—309).—The reaction described by Bamberger and Berlé, in which secondary benziminazoles yield dibenzoyl-*o*-phenylenediamine and a fatty acid by treatment with benzoyl chloride and aqueous sodium hydroxide, is explained by the author's experiments on the benzoylation of secondary or tertiary benziminazoles. He finds that secondary benziminazoles yield a benzoyl derivative. This benzoyl derivative or, in the case of a tertiary compound, the benziminazole itself forms an additive compound with benzoic acid, which probably has the constitution $\text{C}_6\text{H}_4 \text{---} \text{N} \begin{array}{l} \text{NR} \cdot \text{COR}' \\ \text{NHBz} \end{array}$, and is decomposed by the alkali, yielding benzoylated *o*-phenylenediamines and a fatty acid.

[With R. GRÜN and F. KOLASIUS.]—The benziminazoles are treated with benzoyl chloride (2 or 4 mols.) and 10% sodium hydroxide (4 or 6 mols.). The precipitate is treated with ether, whereby the benzoyl derivative and oily products are dissolved; the residue is separated by chloroform into the acylphenylenediamine and dibenzoyl-*o*-phenylenediamine.

Benziminazole yields 1-benzoylbenziminazole (in very small amount), dibenzoyl-*o*-phenylenediamine, and *dibenzoylformyl-o*-phenylenediamine, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{NBz} \cdot \text{CHO}$, m. p. 155—156°, needles, which is converted into formic acid and dibenzoyl-*o*-phenylenediamine by boiling

with alcohol, hydrochloric acid, or sodium hydroxide, and yields, by heating at 180—200°, carbon monoxide, benzoic acid, dibenzoyl-*o*-phenylenediamine, and 1-benzoylbenziminazole.

2-Methylbenziminazole yields 1-benzoyl-2-methylbenziminazole



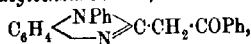
m. p. 86°, long needles, dibenzoyl-*o*-phenylenediamine, and *dibenzoyl-acetyl-o*-phenylenediamine, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{NBzAc}$, m. p. 154°, prisms, which is converted into acetic acid and dibenzoyl-*o*-phenylenediamine by alcoholic hydrochloric acid or sodium hydroxide. 2-Ethylbenziminazole yields similar products; 1-benzoyl-2-ethylbenziminazole, colourless plates, has m. p. 89°, whilst *dibenzoylpropionyl-o*-phenylenediamine, m. p. 124°, yields propionic acid and dibenzoyl-*o*-phenylenediamine by treatment with sodium hydroxide or hydrochloric acid.

1-Phenyl-2-ethylbenziminazole, $\text{C}_6\text{H}_4 \begin{array}{c} \nwarrow \text{NPh} \\ \nearrow \text{N} \end{array} \text{CEt}$, m. p. 45°, colour-

less plates (*hydrochloride*, $\text{C}_{15}\text{H}_{14}\text{N}_2 \cdot \text{HCl} \cdot \text{H}_2\text{O}$, prisms), is prepared by warming *o*-aminodiphenylamine with propionic anhydride and treating the resulting *o*-propionylaminodiphenylamine, $\text{C}_{15}\text{H}_{16}\text{ON}_2$, m. p. 144°, needles, with 10% hydrochloric acid; by treating the solution with sodium carbonate the benziminazole is precipitated. By the action of benzoyl chloride and 10% sodium hydroxide at 50°, it yields an oil and *propionyl-o*-benzoylaminodiphenylamine, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{NPh} \cdot \text{COEt}$, m. p. 157°, plates, which is converted by warm alcoholic potassium hydroxide into propionic acid and *o*-benzoylaminodiphenylamine.

By treatment with benzoyl chloride and 10% sodium hydroxide at 50—60°, 1-phenyl-2-methylbenziminazole yields *acetyl-o*-benzoylaminodiphenylamine, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{NPhAc}$, m. p. 122° (which is decomposed into acetic acid and *o*-benzoylaminodiphenylamine by hot alcoholic sodium hydroxide), a substance, $\text{C}_{28}\text{H}_{20}\text{O}_2\text{N}_2$, m. p. 165°, needles, and an oil which yields the substance, m. p. 165°, by further benzoylation.

The substance, m. p. 165°, is possibly $\text{C}_6\text{H}_4 \begin{array}{c} \nwarrow \text{NPh} \\ \nearrow \text{N} \end{array} \text{C} \cdot \text{CH} : \text{CPh} \cdot \text{OBz}$ since it does not develop a coloration with ferric chloride, and is converted in hot alcoholic solution, by elimination of a benzoyl group, into 1-phenyl-2-phenacylbenziminazole,

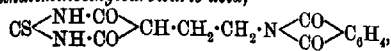


m. p. 119°, large plates or prisms. The latter develops a green coloration with ferric chloride, yields the substance, m. p. 165°, by benzoylation, and forms a *hydrochloride*, m. p. 240—245° (decomp.), *semicarbazone*, m. p. 202°, colourless prisms, and *phenylhydrazone*, m. p. 164°, colourless prisms. C. S.

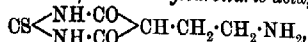
Pyrimidines. LXIII. A New Method of Synthesising Uramils and Thiouramils. TREAT B. JOHNSON and NORMAN A. SHEPARD (*J. Amer. Chem. Soc.*, 1913, 35, 994—1007).—Ethyl phthaliminomalonate reacts with thiocarbamide in warm alcoholic solution containing sodium ethoxide, the product being 2-thiouramil, $\text{CS} \begin{array}{c} \nwarrow \text{NH} \cdot \text{CO} \\ \nearrow \text{NH} \cdot \text{CO} \end{array} \text{CH} \cdot \text{NH}_2$, which is probably formed by the hydrolysis of a previous condensation product; thiouramil when warmed with

sodium hydroxide solution undergoes hydrolysis, giving a substance, possibly *aminothiomalonuric acid*, $\text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$.

Ethyl β -phthaliminoethylmalonate also condenses with thiocarbamide in the presence of sodium ethoxide in hot alcoholic solution, forming 2-thio-5- β -phthaliminoethylbarbituric acid,

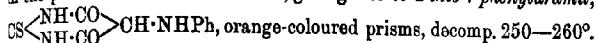


prisms, decomp. $265-270^\circ$ (sodium salt, bright yellow), which on hydrolysis yields 2-thio-5- β -aminoethylbarbituric acid,



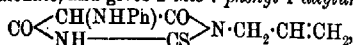
prisms, decomp. $298-300^\circ$, together with phthalic acid. If the condensation is effected with carbamide in place of thiocarbamide, phthalimide and 2:4:6-triketo-5- β -hydroxyethylpyrimidine (5-hydroxy-ethylbarbituric acid), $\text{CO} \begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} \text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, a pale yellow powder which did not melt below 300° , were obtained.

Ethyl anilinomalonate also readily reacts with thiocarbamide in the presence of sodium ethoxide, giving rise to 2-thio-7-phenyluramil,



With carbamide, however, a new type of compound was obtained, namely, *anilinomalonuric acid*, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{NHPh})\cdot\text{CO}_2\text{H}$, prismatic crystals, which do not melt below 300° . This substance when digested with acetic acid undergoes dehydration to γ -phenyluramil,

$\text{CO} \begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} \text{CH}\cdot\text{NHPh}$, an insoluble, crystalline powder. Allylthiocarbamide resembles thiocarbamide in behaving normally with ethyl anilinomalonate, and gives 2-thio-7-phenyl-1-allyluramil,



an insoluble powder, m. p. $185-187^\circ$ (decomp.); sodium salt, brown powder.

When ethyl anilinomalonate is added to an alcoholic solution of sodium ethoxide, it gives a sodium derivative, which on the further addition of *p*-nitrobenzyl chloride reacts with the formation of two substances, one of which is insoluble in ether; the insoluble substance, needles or prisms, m. p. $180-182^\circ$, is probably 2-*p*-nitrobenzylindoxyl,

$\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \text{NH} \end{array} \text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, whilst the soluble substance is ethyl *p*-nitrobenzylanilinomalonate, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}(\text{NHPh})(\text{CO}_2\text{Et})_2$, an oil, which on hydrolysis yields *p*-nitrobenzylanilinomalonic acid, prisms or leaflets, m. p. $205-210^\circ$ (decomp.). D. F. T.

Pyrimidines. LXIV. Synthesis of 4-Methyl-5-ethyl-cytosine. TREAT B. JOHNSON and GEORGE C. BAILEY (*J. Amer. Chem. Soc.*, 1913, 35, 1007-1014).—The paper commences with a summary of the alkyl derivatives of cytosine, $\text{NH} \begin{array}{c} \text{CO}\cdot\text{N} \\ \text{CH}\cdot\text{CH} \end{array} \text{C}\cdot\text{NH}_2$, which have been prepared in the same laboratory.

When warmed together in sodium ethoxide solution, ethyl ethylacetate and thiocarbamide react normally, giving the colourless

sodium salt of 2-thio-4-methyl-5-ethyl-1:2:3:6-tetrahydro-6-pyrimidone, $\text{CS} \begin{smallmatrix} \text{NH} \text{---} \text{CO} \\ \text{NH} \text{---} \text{CMe} \end{smallmatrix} \text{CEt}$, the free substance forming colourless prisms,

m. p. 212°; alkylation is effected when the alcoholic solution of the sodium salt is treated with an alkyl haloid, for example, benzyl chloride gives rise to 2-benzylthiol-4-methyl-5-ethyl-1:6-dihydro-6-pyrimidone, blocks, m. p. 160°, whilst ethyl bromide yields 2-ethylthiol-4-methyl-5-ethyl-1:6-dihydro-6-pyrimidone, colourless crystals, m. p. 138°. The last-named derivative is converted by a molecular proportion of phosphorus pentachloride at 100° into 6-chloro-2-ethylthiol-4-methyl-5-ethylpyrimidine, b. p. 177—180°/21—23 mm., which is stable in contact with water, but is decomposed by warm alcohol, and also reacts with strong alcoholic ammonia at 140—150°, yielding 6-amino-2-ethyl-

thiol-4-methyl-5-ethylpyrimidine, $\text{CEt} \begin{smallmatrix} \text{C}(\text{NH}_2)\text{N} \\ \text{CMe} \text{---} \text{N} \end{smallmatrix} \text{C} \cdot \text{SEt}$, stout blocks, m. p. 89—91°. Both the benzylthiol- and the ethylthiol-substituted pyrimidines described above are converted by hydrolysis with acids into 4-methyl-5-ethyluracil, $\text{CO} \begin{smallmatrix} \text{NH} \text{---} \text{CO} \\ \text{NH} \text{---} \text{CMe} \end{smallmatrix} \text{CEt}$, the yield being

quantitative when the ethylthiol compound is heated with a boiling aqueous solution of chloroacetic acid. The same uracil derivative is obtained in the action of chloroacetic acid on the parent substance, 2-thio-4-methyl-5-ethyl-1:2:3:6-tetrahydro-6-pyrimidone.

2-Ethylthiol-4-methyl-5-ethyl-1:6-dihydro-6-pyrimidone, when heated with aniline at 100° and with alcoholic ammonia at 150—160°, eliminates the thiol group with formation respectively of 2-amino-4-methyl-5-ethyl-1:6-dihydro-6-pyrimidone, $\text{CNHPh} \begin{smallmatrix} \text{NH} \text{---} \text{CO} \\ \text{N} \text{---} \text{CMe} \end{smallmatrix} \text{CEt}$, m. p. 195°, and 2-amino-4-methyl-5-ethyl-1:6-dihydro-6-pyrimidone, prisms, m. p. 281—282° (decomp.); hydrobromide, needles, m. p. 160—175°, according to rate of heating; hydrochloride, m. p. 115°, crystallises with one H₂O.

Boiling hydrochloric acid converts 6-amino-2-ethylthiol-4-methyl-5-ethylpyrimidine into 6-amino-4-methyl-5-ethyl-2:3-dihydro-2-pyrimidone (methylthylecytosine), $\text{CO} \begin{smallmatrix} \text{N} \text{---} \text{C}(\text{NH}_2) \\ \text{NH} \text{---} \text{CMe} \end{smallmatrix} \text{CEt}$, blocks or rectangular prisms, m. p. 295° (decomp.), which is obtained first as the hydrochloride, a colourless powder, decomp. at 125°; the hydrobromide, blocks, decomp. near 260°; the picrate, needles, mercurichloride, phosphotungstate, and potassium-bismutho-iodide were also prepared.

The sodium salt of 2-thio-4-methyluracil reacts with diphenylmethyl bromide in alcoholic solution with formation of 2-diphenylmethylthiol-4-methyl-1:6-dihydro-6-pyrimidone, $\text{CH} \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{CMe} \text{---} \text{N} \end{smallmatrix} \text{C} \cdot \text{S} \cdot \text{CHPh}_2$, m. p. 214°, in small yield.

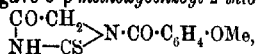
D. F. T.

Hydantoins. XXIII. Synthesis of 2-Thiohydantoins from Acyl Derivatives of α -Amino-acids. TREAT B. JOHNSON and WALTER M. SCOTT (*J. Amer. Chem. Soc.*, 1913, 35, 1130—1136. Compare JOHNSON, A., 1912, i, 390; JOHNSON and NICOLET, A., 1912, i, 53, etc.). —The reaction between ammonium thiocyanate and an acyl derivative

of an α -amino-acid in acetic anhydride solution appears to be a general one, but the only β -amino-acid examined merely underwent acetylation without any subsequent reaction with the thiocyanate.

α -Carboxybenzoylaminoacetic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, obtained by the hydrolysis of ethyl phthalylaminoacetate, when heated by steam for twenty minutes with a $1\frac{1}{2}$ molecular proportion of ammonium thiocyanate in 5–7 parts by weight of acetic anhydride, gave 2-thiohydantoin, m. p. $225\text{--}227^\circ$, phthalylaminoacetic acid, m. p. $192\text{--}193^\circ$, and phthalic acid. This was the only case in which the acylhydantoin could not be isolated, although the results indicate that it must have been an intermediate product of the reaction.

p -Methoxyhippuric acid with ammonium thiocyanate in acetic anhydride solution gave 3- p -methoxybenzoyl-2-thiohydantoin,



pale yellow prisms, m. p. 166° , whilst m -nitrohippuric acid yielded 3- m -nitrobenzoyl-2-thiohydantoin, m. p. $198\text{--}199^\circ$.

Benzenesulphonylaminoacetic acid in an analogous manner gave rise to 3-benzenesulphonyl-2-thiohydantoin, $\begin{array}{c} \text{CO}\cdot\text{CH}_2 \\ | \\ \text{NH}-\text{CS} \end{array} \text{N}\cdot\text{SO}_2\text{Ph}$, colourless needles, m. p. $210\text{--}211^\circ$ (decomp.).

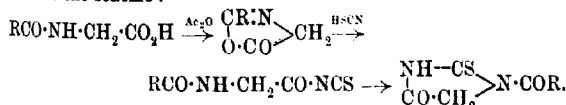
The product obtained by a similar process with carbethoxyaminoacetic acid was ethyl 2-thiohydantoin-3-carboxylate, $\begin{array}{c} \text{CO}\cdot\text{CH}_2 \\ | \\ \text{NH}-\text{CS} \end{array} \text{N}\cdot\text{CO}_2\text{Et}$, plates, m. p. 168° .

The application of dibromophenylalanine and benzoylalanine to this reaction resulted in the formation of 2-thio-3-acetyl-4-dibromobenzylhydantoin, $\begin{array}{c} \text{NH}-\text{CO} \\ | \\ \text{CS}\cdot\text{NAc} \end{array} \text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3\text{Br}_2$, plates, m. p. 171° (which on hydrolysis gave 2-thio-4-dibromobenzylhydantoin, colourless needles, m. p. 243°), and 2-thio-3-benzoyl-4-methylhydantoin, m. p. 158° respectively.

Anthranilic acid under similar treatment merely became converted into acetylanthranilic acid.

D. F. T.

Hydantoins. XXIV. Action of Ammonium Thiocyanate on Lactone Anhydrides of Acylamino-acids. TREAT B. JOHNSON and WALTER M. SCOTT (*J. Amer. Chem. Soc.*, 1913, 35, 1136–1143. Compare preceding abstract).—The provisional interpretation of the mechanism of the reaction between thiocyanic acid (as ammonium thiocyanate) and the acyl derivative of a monobasic α -amino-acid in acetic anhydride (Johnson and Nicolet, A., 1912, i, 53) is withdrawn in favour of the scheme :



Among the reasons for this new view are the facts that acetic anhydride is the only solvent which has been found suitable, and that

the first ring formation is a normal change when acylamino-acids are heated with acetic anhydride; it has already been shown that the lactonoid anhydrides undergo scission by hydrogen chloride, producing acid chlorides in a manner analogous to the second change above (compare Mohr and Kohler, A., 1910, i, 116).

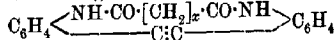
In agreement with the above explanation it is found that with hippuric acid or benzoylalanine, acylthiohydantoins are not produced in acetic acid with ammonium thiocyanate, although if the amino-acid is previously heated with acetic anhydride the resulting lactonoid anhydride readily gives rise to the corresponding acylthiohydantoin in acetic acid solution.

Acetylphenylglycine and ethyl hippurate are not affected by ammonium thiocyanate in acetic anhydride, thus indicating the necessity for the presence of unsubstituted hydrogen at the nitrogen atom and at the carboxyl group. With benzamide, no evidence of the formation of benzoylthiocarbamide was obtained; this is a further reason for discarding the old theory of formation in favour of that now suggested.

Contrary to expectation, the lactim of α -benzoylamino- β -phenylacrylic acid failed to react with thiocyanic acid in acetic anhydride, whilst the free acid under such treatment only yielded the lactim.

D. F. T.

Rings Containing a Triple Linking. II. Optimum Number of Atoms in the Ring. PAUL RUGGLI (*Annalen*, 1913, 399, 174—182).—The following substances of the type



have been prepared from *oo*'-diaminotolan and the requisite acid chloride in the same manner as *cyclosuccinyldiaminotolan* (A., 1912, i, 914); *cycloglutaryldiaminotolan*, $\text{C}_{19}\text{H}_{16}\text{O}_2\text{N}_2$, m. p. 300—302° (decomp.), colourless crystals, *cycloadipyldiaminotolan*, $\text{C}_{20}\text{H}_{18}\text{O}_2\text{N}_2$, m. p. 252° (decomp.), colourless needles, *cyclopimelyldiaminotolan*, $\text{C}_{21}\text{H}_{20}\text{O}_2\text{N}_2$, m. p. 248° (decomp.), colourless needles, *cyclosuberyldiaminotolan*, $\text{C}_{22}\text{H}_{22}\text{O}_2\text{N}_2$, m. p. 223—224.5°, colourless needles, and *cyclolepargyldiaminotolan*, $\text{C}_{22}\text{H}_{24}\text{O}_2\text{N}_2$, m. p. about 240° (decomp.), colourless needles.

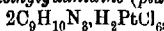
A comparison of the yields obtained under similar conditions shows *cycloadipyldiaminotolan*, containing a 14-membered ring, is obtained in the largest amount, namely, 50% of that theoretically possible. Cyclic compounds containing a nuclear triple linking have not been obtained from *pp*'-diaminotolan or from *trans-oo*'-diaminostilbene.

pp'-Dinitrotolan, which is best prepared by boiling *pp*'-dinitrostilbene dibromide with pyridine, is readily reduced to *pp*'-diaminotolan by stannous chloride and hydrochloric and acetic acids in the cold.

C. S.

Benzylcreatinine. WILLY HENNIG (*Arch. Pharm.*, 1913, 251, 396—400).—Creatinine and benzyl chloride at 136—140° yield *benzylcreatinine hydrochloride*, $\text{C}_{11}\text{H}_{13}\text{ON}_3\text{HCl}$, faintly yellow needles, blackening at about 230° (*aurichloride*, $\text{C}_{11}\text{H}_{13}\text{ON}_3\text{HAuCl}_4$, m. p. 158°, yellow needles; *platinichloride*, $2\text{C}_{11}\text{H}_{13}\text{ON}_3\text{H}_2\text{PtCl}_6$, m. p.

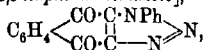
177—178°, red crystals), from an aqueous solution of which lead hydroxide liberates *benzylcreatinine*, m. p. 225°, faintly yellow crystals. The action, therefore, of benzyl chloride, similarly to that of alkyl iodides, on creatinine is substitutive, not additive. The oxidation of benzylcreatinine hydrochloride by alkaline 5% potassium permanganate at 30—40° yields *benzylmethylguanidine* (*platinichloride*,



m. p. 148°; *aurichloride*, m. p. 190—191°).

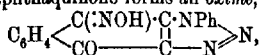
C. S.

Addition of Phenylazoimide to Quinones. II. LUDWIG WOLFF (*Annalen*, 1913, 399, 274—297).—[With R. HERCHER.]— α -Naphthaquinone and phenylazoimide react to form a dihydrotriazole derivative, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{CH}\cdot\text{NPh} \\ \text{CO}\cdot\text{CH}\cdot\text{N} \end{smallmatrix}\text{N}$, which cannot be isolated, but decomposes, yielding mainly 1-phenylazoimino- α -naphthaquinone [4:9-diketo-1-phenyldihydro- $\beta\beta$ -naphthaisotriazole],



m. p. 241°, pale yellow leaflets, at 60—65°, and mainly indandione-2-aldehydeanil, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\text{CH}\cdot\text{CH}\cdot\text{NPh}$, m. p. 191°, yellow prisms or plates, on the water-bath.

Phenylazoiminonaphthaquinone forms an *oxime*,



m. p. 232° (decomp.), almost colourless needles, which probably contains the oximino-group in the position shown, because, unlike the parent substance, it is not ruptured by sodium hydroxide. Phenylazoiminonaphthaquinone itself is decomposed by boiling aqueous alcoholic sodium hydroxide, yielding after acidification 4-*o*-carboxy-

benzoyl-1-phenyl-1:2:3-triazole, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{NPh} \\ \text{N}=\text{N} \end{smallmatrix}$, m. p.

177—178° (anhydrous), colourless needles containing $\frac{1}{2}\text{H}_2\text{O}$. This acid is decomposed into phthalic acid, aniline, and probably acetic acid by aqueous sodium hydroxide at 150°, and in alkaline solution yields with hydroxylamine hydrochloride and subsequent acidification the oxime of the acid, which, however, slowly changes to an *anhydride*, $\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_4$, m. p. 220°, colourless needles, insoluble in sodium carbonate.

Indandione-2-aldehydeanil does not develop a coloration with ferric chloride, forms a *sodium* salt, red needles, with alcoholic sodium hydroxide, and is decomposed by boiling aqueous sodium hydroxide, yielding aniline and indandione-2-aldehyde in the form of its *sodium* salt, $\text{C}_{10}\text{H}_6\text{O}_2\text{Na}$, yellow needles. Indandione-2-aldehyde crystallises in colourless needles containing H_2O , m. p. 125° (decomp.) (141°, anhydrous), develops a red coloration with ferric chloride, and behaves like a strong, monobasic acid, decomposing carbonates; the *calcium* salt crystallises in sparingly soluble prisms. The aldehyde or its salt in cold aqueous solution reacts with aniline, phenylhydrazine, hydroxylamine, and semicarbazide to form respectively the preceding anil;

phenylhydrazones, $C_{16}H_{19}O_2N_2$, m. p. 220° (decomp.), yellow prisms; *oxime*, $C_{10}H_7O_3N, H_2O$, m. p. 205° (decomp.), orange needles, and *semicarbazone*, $C_{11}H_9O_3N_3$, m. p. 233° (decomp.), yellow needles.

By boiling with 20% hydrochloric acid, the sodium salt of indandione-2-aldehyde is decomposed into formic acid, bindone, indandione, and a substance, $C_{19}H_{10}O_4$, m. p. about 308° (decomp.), red needles, which is probably $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C:CH:CH \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_4$, since it can also be produced by heating equal molecular quantities of indandione and its aldehyde at 120° or in boiling alcohol, and can be converted into these two substances by aqueous sodium hydroxide.

[With M. KÖRBS].—Three of the four substances produced by the interaction of phenylazoisimide and *p*-benzoquinone have been previously described (A., 1912, i, 1034). The fourth is a substance, $C_{18}H_{14}O_2N_4$, m. p. $157-160^\circ$ (decomp.), yellow leaflets, the constitution of which has not yet been entirely established. The author recommends the formula $N \begin{smallmatrix} \diagup NPh \cdot CH \cdot CO \\ \diagdown N \end{smallmatrix} \begin{smallmatrix} \diagup CH \cdot CO \\ \diagdown CH \cdot CO \end{smallmatrix} CH:CH:NPh$, according to which the substance is the *anil* of *phenylazoisiminopentialdehyde*. The absence of an imino-group and the presence of a triazole ring are respectively proved by the inactivity of the substance towards phenylcarbimide and by the oxidation of the sodium salt of phenylazoisiminopentialdehyde to 1-phenyl-1:2:3-triazole-4-carboxylic acid and 1-phenyl-1:2:3-triazole-5-carboxylic acid by 2% sodium hypobromite at 0° . The presence of the C_6 -ring in the anil has not been proved, but is rendered very probable by the great similarity of the substance to the anil of indandione-2-aldehyde in its method of formation and behaviour.

By treatment with 10% potassium hydroxide and a little alcohol at $30-40^\circ$, the anil is converted into the *potassium* salt of phenylazoisiminopentialdehyde, $C_{12}H_8O_3N_3K, \frac{1}{2}H_2O$, colourless prisms which become yellow in light; the *sodium* salt, $C_{12}H_8O_3N_3Na, H_2O$, crystallises in colourless leaflets, and forms a *semicarbazone*, $C_{13}H_{11}O_3N_4Na, 2\frac{1}{2}H_2O$, faintly yellow needles. These salts and also the semicarbazone are extensively decomposed by treatment with even weak acids.

By fusion or by boiling with xylene or aniline, the anil of phenylazoisiminopentialdehyde loses nitrogen and yields a substance,

$C_{18}H_{14}O_2N_2$, m. p. 185° , colourless needles, which behaves very similarly to the original anil and is, therefore, probably the *anil* of *phenyliminopentialdehyde*, $NPh \begin{smallmatrix} \diagup CH \cdot CO \\ \diagdown CH \cdot CO \end{smallmatrix} CH:CH:NPh$. It does not react with

phenylcarbimide or with ferric chloride, and is converted by boiling sodium hydroxide into aniline and the *sodium* salt of *phenyliminopentialdehyde*, $C_{12}H_8O_3NNa, 2H_2O$, white needles.

By keeping phenylazoisiminopentialdehydeanil in glacial acetic acid until the evolution of nitrogen ceases, a substance, $C_{18}H_{16}O_3N_2$, m. p. about 186° (decomp.), yellow, crystalline powder, is obtained, which is converted by hot aqueous alcoholic sodium hydroxide into aniline and the *sodium* salt of an acid, $C_{17}H_{12}O_4N$, m. p. 234° , colourless needles.

C. S.

3:6-Diamino-1:2:4:5-tetrazine. I. GIACOMO PONZIO and G. GASTALDI (*Gazzetta*, 1913, 43, ii, 129—137).—3:6-Diamino-1:2:4:5-tetrazine, $\text{H}_2\text{N}\cdot\text{C}\begin{smallmatrix} \text{N:N} \\ \text{N:N} \end{smallmatrix}\text{C}\cdot\text{NH}_2\cdot\text{H}_2\text{O}$, begins to crystallise in a few

days when a mixture of concentrated solutions of aminoguanidine hydrochloride and potassium hydroxide are kept over concentrated sulphuric acid and solid potassium hydroxide. The substance crystallises in reddish-violet, monoclinic needles, which have a metallic lustre, or in amethyst-coloured laminae. On heating, it loses water at about 100° , and melts at $204\text{--}205^\circ$ (decomp.), or $206\text{--}207^\circ$ (decomp.), according to the mode of heating; cyanogen and ammonia are evolved. When boiled with sulphuric acid, it yields nitrogen, carbon dioxide, and hydrazine sulphate, whilst heating with potassium hydroxide furnishes ammonia. It is readily reduced to 3:6-diamino-1:2-dihydro-1:2:4:5-tetrazine.

3:6-Diamino-1:2:4:5-tetrazine hydrochloride, $\text{C}_2\text{H}_4\text{N}_6\cdot\text{HCl}$, forms orange-yellow laminae, and decomposes about 200° ; the nitrate, $\text{C}_2\text{H}_4\text{N}_6\cdot\text{HNO}_3\cdot\frac{1}{2}\text{H}_2\text{O}$, crystallises similarly, and has m. p. $180\text{--}182^\circ$ (decomp.). The oxalate, $(\text{C}_2\text{H}_4\text{N}_6)_2\cdot\text{H}_2\text{C}_2\text{O}_4$, forms orange prisms, which decompose at about 205° . R. V. S.

Action of Dichlorocarbamide on Amines. Synthesis of 3-Hydroxy-6-keto-3-phenyl-2:4-dibenzyl-1:2:4:5-tetrazine. RASIK LAL DATTA and SATYARANJAN DAS GUPTA (*J. Amer. Chem. Soc.*, 1913, 35, 1183—1185).—By modifying the conditions for the interaction of dichlorocarbamide and amines, which has already been shown to yield chloroamines (Datta, T., 1912, 101, 166; A., 1912, i, 962), it is found that other substances can be isolated from the reaction product.

When a cooled saturated solution of dichlorocarbamide is added to a cooled fairly strong aqueous solution of allylamine, a small amount of *p*-urazine separates.

On applying benzylamine in a similar reaction the crystalline product which deposits is a mixture of *p*-urazine with 3-hydroxy-6-keto-3-phenyl-2:4-dibenzyl-1:2:4:5-tetrazine. The latter, which can be separated by its greater solubility in acetone, probably owes its formation to the primary formation of benzylchloroamine, two molecules of which then condense with one of free benzylamine and one of dichlorocarbamide.

D. F. T.

The Solubility of Uric Acid in Acetic Acid. FRANCESCO ROSSI (*Biochem. Zeitsch.*, 1913, 54, 297—304).—The solubility of uric acid in varying strengths of acetic acid from $N/100$ to $16N$ (glacial acetic acid) and at temperatures varying from 15° to 100° was determined. Between the concentrations $N/100$ and $N/10$ the solubility is less than in water; above the latter concentration it increases and reaches a maximum somewhere about the concentration of $4N$ to $6N$; in higher concentrations, the solubility again declines, especially at higher temperatures. The latter phenomenon is probably due to an action of acetic acid on the uric acid.

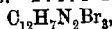
S. B. S.

Some New Derivatives of Azoxybenzene. BRUNO VALORI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 125—133. Compare Angeli and Valori, A., 1913, i, 533).—When Zinin's *p*-nitroazoxybenzene is treated with nitric acid (D 1.48) on the water-bath, 2:4-dinitroazoxybenzene, $C_6H_3(NO_2)_2 \cdot N \cdot NPh \cdot O$, is produced; it forms pale yellow needles, m. p. 141°.

When Zinin's *p*-nitroazoxybenzene is heated with bromine in presence of iron for one hour at 130° in a sealed tube, 2-bromo-4-nitroazoxybenzene, $NO_2 \cdot C_6H_3Br \cdot N \cdot NPh \cdot O$, is formed; it is a yellow powder, m. p. 127°.

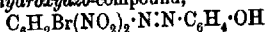
o-Nitroazoxybenzene is acted on by nitric acid (D 1.48) on the water-bath, yielding 2:6-dinitroazoxybenzene, $C_{12}H_8O_5N_4$, which forms colourless scales, m. p. 172°.

If *o*-*p*-bromoazoxybenzene is heated with bromine in presence of iron in a sealed tube for two hours at 115—120°, 2:4-dibromoazoxybenzene, $C_{12}H_8ON_2Br_2$, is formed; it crystallises in yellow needles, m. p. 97°. In its preparation a small quantity of 2:4:6-tribromoaniline is produced. Reduction of 2:4-dibromoazoxybenzene with tin and hydrochloric acid yields aniline and 2:4-dibromoaniline. 2:4-Dibromoazoxybenzene yields 2:4-dibromoazobenzene, $C_{12}H_8N_2Br_2$, when treated with concentrated sulphuric acid, or when reduced with aluminium amalgam and subsequently oxidised with yellow mercury oxide. 2:4-Dibromoazobenzene forms orange-red prisms, m. p. 96°. It regenerates the azoxy-compound when treated with hydrogen peroxide in glacial acetic acid solution. 2:4:4'-Tribromoazobenzene,

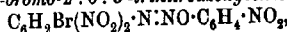


can be obtained by warming dibromoazobenzene with bromine and iron for a few minutes on the water-bath; it is a pale red substance, m. p. 146°. On oxidation with hydrogen peroxide in glacial acetic acid solution, this compound yields the corresponding 2:4:4'-tribromoazoxybenzene, which on reduction with aluminium amalgam and subsequent oxidation with yellow mercury oxide yields the tribromoazo-compound again. 2:4:4'-Tribromoazoxybenzene, $C_{12}H_7ON_2Br_3$, crystallises in yellow needles, m. p. 154°.

When 4-bromo-2-nitroazoxybenzene (m. p. 99°) is heated on the water-bath with nitric acid (D 1.50) two products are obtained: (1) 4-bromo-2:6-dinitroazoxybenzene, which forms very pale yellow needles, m. p. 163°, and on treatment with concentrated sulphuric acid yields the isomeric hydroxyazo-compound,



(m. p. 224°); (2) 4-bromo-2:6:3'-trinitroazoxybenzene,



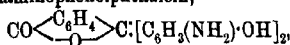
which is a yellowish-green, crystalline powder, m. p. 209° (decomp.). The latter compound is exclusively formed if stronger acid (D 1.52) is used in the reaction. R. V. S.

Phthaleins. II. Some Nitrogenous Derivatives of Phenolphthalein and the Constitution of its Salts. BERNARDO ODDO (*Gazzetta*, 1913, 43, ii, 175—190. Compare Oddo and Vassallo, A., 1912, i, 792).—Bis-*p*-toluenearazophenolphthalein (formula overleaf) is obtained when a diazotised solution of *p*-toluidine (1 mol.) is poured

into a cold solution of phenolphthalein ($\frac{1}{2}$ mol.) in potassium hydroxide (3 mols.). It is an orange-yellow, crystalline substance, m. p. 249—253°. When the mother-liquor is acidified, a bright red substance, m. p. 207—210°, is precipitated; the *acetyl* derivative of this compound forms pale yellow scales, m. p. 148—150°. The *diacetyl* derivative of bis-*p*-tolueneazophenolphthalein, $C_{38}H_{30}O_6N_4$, has m. p. 125—131°.

Bis-o-nitrobenzeneazophenolphthalein, $C_{32}H_{20}O_8N_6$, is an orange-yellow substance, m. p. 277°. Its *diacetyl* derivative has m. p. 124—129°. In the preparation of bis-*o*-nitrobenzeneazophenolphthalein, a substance of similar appearance but different solubility is formed; its *acetyl* derivative has m. p. 169°.

When bis-*p*-tolueneazophenolphthalein is heated to 110° with phenylhydrazine, a reaction occurs, which is accompanied by rise of temperature and yields diaminophenolphthalein,



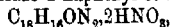
which forms pale coffee-coloured crystals, m. p. 245° (decomp.). The substance dissolves in alkalis, alkali carbonates and ammonia, giving a Prussian-blue coloration which disappears on acidification. The substance gives the same coloration with aqueous solutions of pyridine, but not with alcoholic solutions. Diaminophenolphthalein can also be obtained by reduction of dinitrophenolphthalein with stannous chloride (compare Errera and Berté, A., 1896, i, 564; Gattermann and Bamberg, A., 1899, i, 514).

Dinitrophenolphthalein yields a *monoacetyl* derivative, $C_{34}H_{16}O_{10}N_2$, which has m. p. 94—100°, and occurs in a white and in a yellow form.

R. V. S.

Mechanism of Formation and Scission of the Hydroxyazo-compounds. G. CHARBIER and G. FERRERI (*Gazzetta*, 1913, 43, ii, 148—162. Compare this vol., i, 535).—When an ethereal solution of nitric acid (prepared by adding about 20% of nitric acid [D 1.48] to ether cooled in ice) is added to an ethereal solution of 1-benzeneazo-2-naphthyl methyl ether, the *nitrate* of the ether, $C_{17}H_{14}ON_2 \cdot 2HNO_3$, separates in red, silky needles, m. p. 67° (decomposing with evolution of gas at 69—70°). The salt has about the normal molecular weight in boiling chloroform. It is hydrolysed by water. The salt readily decomposes into benzenediazonium nitrate and 1-nitro-2-naphthyl methyl ether.

The *nitrate* of 1-benzeneazo-2-naphthyl ethyl ether,



forms quadrangular tablets, which are green by reflected and red by transmitted light, and have m. p. 80—81° (decomp.). It readily decomposes in an analogous manner to the methyl ether nitrate.

When 1-nitro-2-naphthyl ethyl ether is warmed with nitric acid

(D 140), it is converted quantitatively into 1:6-dinitro-2-naphthyl ethyl ether.

A dark red, crystalline crust, consisting probably of 1-benzeneazo-2-naphthol nitrate, is obtained after mixing ethereal nitric acid with an ethereal solution of 1-benzeneazo-2-naphthol. The substance is very unstable.

The probable structure of these salts is indicated by the annexed formula, and their mode of decomposition mentioned above suggests an analogous mechanism of formation and scission of the hydroxyazo-compounds.

R. V. S.

Etherification of o-Hydroxyazo-compounds. III. G. CHARRIER and G. FERRERI (*Gazzetta*, 1913, 43, ii, 211—227. Compare A., 1912, i, 812; this vol., i, 535, and preceding abstract).—In this paper further nitrates of ethers of arylazo- β -naphthols are described. Their chemical and physical properties resemble those of the members already described (*loc. cit.*).

1-o-Tolueneazo-2-naphthyl methyl ether nitrate, $C_{18}H_{16}ON_2 \cdot 2HNO_3$, forms cantharides-green, acicular crystals, m. p. 71° (decomp.).

1-o-Tolueneazo-2-naphthyl ethyl ether nitrate, $C_{19}H_{18}ON_2 \cdot 2HNO_3$, crystallises in cantharides-green leaflets, m. p. $62-63^\circ$ (decomp.).

1-m-Tolueneazo-2-naphthyl methyl ether nitrate, $C_{18}H_{18}ON_2 \cdot 2HNO_3$, crystallises similarly, and has m. p. 72° (decomp.).

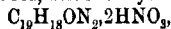
1-m-Tolueneazo-2-naphthyl ethyl ether nitrate, $C_{19}H_{18}ON_2 \cdot 2HNO_3$, forms cantharides-green leaflets, m. p. 84° (decomp.).

1-p-Tolueneazo-2-naphthyl methyl ether hydrochloride forms red needles which have a golden lustre. The hydrobromide crystallises in metallic-looking, green leaflets. The nitrate, $C_{18}H_{16}ON_2 \cdot 2HNO_3$, forms dark red needles with a green lustre, and has m. p. 77° (decomp.).

1-p-Tolueneazo-2-naphthyl ethyl ether nitrate, $C_{19}H_{18}ON_2 \cdot 2HNO_3$, crystallises in garnet-red leaflets of golden lustre, and has m. p. 94° (decomp.).

1-o-4-Xyleneazo-2-naphthol, $C_{18}H_{16}ON_2$, crystallises in cherry-red needles of golden lustre, m. p. 146° ; it dissolves in concentrated sulphuric acid, producing an intense red coloration. The methyl ether, $C_{19}H_{18}ON_2$, crystallises in red, prismatic leaflets, m. p. 106° . The methyl ether hydrochloride forms red needles with golden lustre; the hydrobromide, garnet-red needles. The nitrate, $C_{19}H_{18}ON_2 \cdot 2HNO_3$, forms coffee-coloured scales of golden lustre, m. p. $87-88^\circ$ (decomp.). The ethyl ether, $C_{20}H_{20}ON_2$, forms red needles of golden lustre, m. p. $94-95^\circ$. The ethyl ether hydrochloride forms metallic-looking, coffee-coloured needles; the hydrobromide, red needles.

1-m-4-Xyleneazo-2-naphthyl methyl ether, $C_{19}H_{18}ON_2$, forms garnet-red leaflets of violet lustre, m. p. $72-73^\circ$. The hydrochloride and hydrobromide form garnet-red, acicular crystals. The nitrate,



crystallises in cantharides-green needles, m. p. 83° (decomp.).

²⁸ m-4-Xylenediazonium nitrate and 2-naphthylamine yield 1-m-4-xylene-

azo-2-naphthylamine, $C_{18}H_{17}N_3$, which crystallises in orange-red leaflets, m. p. 128° . The substance dissolves in concentrated sulphuric acid, producing a reddish-violet coloration.

1-m-4-*Xyleneazo-2-naphthyl ethyl ether*, $C_{20}H_{20}ON_2$, forms garnet-red needles, m. p. 47° . The *hydrochloride* forms coffee-coloured needles, and the *hydrobromide*, garnet-red needles. The *nitrate*,

$C_{20}H_{20}ON_2 \cdot 2HNO_3$, crystallises in cantharides-green needles, m. p. 82° (decomp.).

1-p-*Xyleneazo-2-naphthyl methyl ether*, $C_{19}H_{18}ON_2$, forms garnet-red, prismatic tablets, m. p. $91-92^\circ$. The *hydrochloride* crystallises in garnet-red needles; the *hydrobromide* in coffee-coloured needles. The *nitrate*, $C_{19}H_{18}ON_2 \cdot 2HNO_3$, crystallises in cantharides-green laminae, m. p. 75° (decomp.). The *ethyl ether*, $C_{20}H_{20}ON_2$, crystallises in tufts of red needles or laminae, m. p. $61-62^\circ$. The *hydrochloride* forms a crust of copper-coloured needles, and the *hydrobromide* crystallises similarly. The *nitrate*, $C_{20}H_{20}ON_2 \cdot 2HNO_3$, forms dark copper-coloured laminae of golden lustre, m. p. 71° (decomp.).

1-o-*Naphthaleneazo-2-naphthyl methyl ether hydrobromide* crystallises in iridescent, brownish-green needles.

R. V. S.

Etherification of *o*-Hydroxyazo-compounds. IV. G. CHARRIER and G. FERRERI (*Gazzetta*, 1913, 43, ii, 227-244. Compare preceding abstracts).—1-*Anisoleazo-2-naphthyl methyl ether hydrobromide* forms reddish-brown needles. The *nitrate*, $C_{18}H_{16}O_2N_2 \cdot 2HNO_3$, forms dark green needles, m. p. $90-91^\circ$ (decomp.). 1-*Anisoleazo-2-naphthylamine*, $C_{17}H_{15}ON_2$, crystallises in garnet-red prisms, m. p. $133-134^\circ$; it is soluble in concentrated sulphuric acid with production of a reddish-violet coloration.

1-*Anisoleazo-2-naphthyl ethyl ether hydrobromide* forms brownish-red needles. The *nitrate*, $C_{19}H_{18}O_2N_2 \cdot 2HNO_3$, is a dark green, crystalline substance, m. p. 85° (decomposing at $86-87^\circ$).

1-p-*Methoxybenzeneazo-2-naphthyl methyl ether hydrobromide* forms cantharides-green needles. The *nitrate*, $C_{18}H_{16}O_2N_2 \cdot 2HNO_3$, forms green, acicular crystals, m. p. $55-56^\circ$ (decomp.). 1-p-*Methoxybenzeneazo-2-naphthylamine*, $C_{17}H_{15}ON_2$, crystallises in garnet-red leaflets, m. p. 127° . It dissolves in concentrated sulphuric acid, giving a violet-red coloration.

1-p-*Methoxybenzeneazo-2-naphthyl ethyl ether hydrobromide* forms coffee-coloured needles. The *nitrate*, $C_{19}H_{18}O_2N_2 \cdot 2HNO_3$, crystallises in cantharides-green leaflets, m. p. 67° (decomp.).

1-o-*Ethoxybenzeneazo-2-naphthyl methyl ether hydrochloride* forms garnet-red crystals; the *hydrobromide*, coffee-coloured needles. The *nitrate*, $C_{19}H_{18}O_2N_2 \cdot 2HNO_3$, crystallises in dark red leaflets of metallic lustre.

1-o-*Ethoxybenzeneazo-2-naphthyl ethyl ether hydrobromide* forms brown needles; the *nitrate*, $C_{20}H_{20}O_2N_2 \cdot 2HNO_3$, crystallises in green needles, m. p. 86° (decomp.). 1-o-*Ethoxybenzeneazo-2-naphthylamine*, $C_{18}H_{17}ON_2$, forms bright red leaflets, m. p. 117° . It dissolves in concentrated sulphuric acid, giving a reddish-violet coloration.

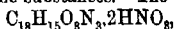
1-p-*Ethoxybenzeneazo-2-naphthyl methyl ether hydrobromide* forma

coffee-coloured needles. The *nitrate*, $C_{15}H_{15}O_5N_3 \cdot 2HNO_3$, forms green needles, m. p. 71° (decomp.). 1-p-*Ethoxybenzeneazo-2-naphthylamine*, $C_{18}H_{17}ON_3$, crystallises in orange-yellow laminae of golden lustre, m. p. $133-134^\circ$.

1-p-*Ethoxybenzeneazo-2-naphthyl ethyl ether hydrobromide* forms golden leaflets. The *nitrate*, $C_{20}H_{20}O_5N_3 \cdot 2HNO_3$, forms orange-yellow plates of golden lustre, m. p. $73-74^\circ$ (decomp.).

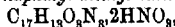
1-o-*Nitrobenzeneazo-2-naphthyl methyl ether*, $C_{17}H_{15}O_3N_3$, crystallises in garnet-red leaflets, m. p. $136-137^\circ$. It dissolves in concentrated sulphuric acid, giving an intense red coloration. The *hydrochloride* forms coffee-coloured needles, and the *hydrobromide* is a pale coffee-coloured, crystalline substance. The *nitrate*, $C_{17}H_{15}O_5N_3 \cdot 2HNO_3$, forms red crystals, m. p. 103° .

1-o-*Nitrobenzeneazo-2-naphthyl ethyl ether*, $C_{18}H_{15}O_5N_3$, crystallises in thin, dark red tablets, m. p. 111° . The *hydrochloride* and the *hydrobromide* are red, crystalline substances. The *nitrate*,



forms dark red leaflets of metallic lustre, m. p. 105° (decomp.).

1-m-*Nitrobenzeneazo-2-naphthyl methyl ether nitrate*,

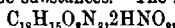


consists of golden leaflets, m. p. $66-68^\circ$ (decomp.).

1-m-*Nitrobenzeneazo-2-naphthyl ethyl ether hydrobromide* is a red, crystalline substance. The *nitrate*, $C_{18}H_{15}O_5N_3 \cdot 2HNO_3$, crystallises in golden leaflets, m. p. 70° (decomp.).

1-p-*Nitrobenzeneazo-2-naphthyl methyl ether*, $C_{17}H_{13}O_3N_3$, forms dark red, iridescent leaflets, m. p. $128-129^\circ$. The *hydrochloride* is a red, and the *hydrobromide* a coffee-coloured, crystalline substance. The *nitrate*, $C_{17}H_{13}O_5N_3 \cdot 2HNO_3$, forms cantharides-green leaflets, m. p. 75° (decomp.).

1-p-*Nitrobenzeneazo-2-naphthyl ethyl ether*, $C_{18}H_{15}O_5N_3$, crystallises in dark red leaflets, m. p. about 186° . The *hydrochloride* and the *hydrobromide* are red, crystalline substances. The *nitrate*,



forms cantharides-green leaflets, m. p. $95-97^\circ$ (decomp.).

1-a-*Naphthaleneazo-2-naphthyl ethyl ether hydrobromide* crystallises in cantharides-green needles. The *nitrate*, $C_{22}H_{18}ON_3 \cdot 2HNO_3$, crystallises in copper-red, flat needles of metallic lustre, m. p. 62° (decomp.).

1- β -*Naphthaleneazo-2-naphthyl methyl ether hydrobromide* crystallises in coffee-coloured needles. The *nitrate*, $C_{22}H_{18}ON_3 \cdot 2HNO_3$, forms deep green, lustrous needles, m. p. $80-81^\circ$ (decomp.).

Diphenyl-4 : 4'-bisazo-2-naphthol,



is a dark green, microcrystalline powder, m. p. about 275° ; it dissolves in concentrated sulphuric acid with production of a violet-blue coloration. Its *diethyl ether*, $C_{26}H_{20}O_2N_4$, is a red, microcrystalline powder, m. p. about $98-100^\circ$. It is soluble in concentrated (and to some extent also in dilute) acids with production of a bluish-violet coloration. The *hydrochloride* and the *hydrobromide* are dark green, crystalline substances. The *nitrate*, $C_{26}H_{20}O_4N_4 \cdot 4HNO_3$, forms dark green needles of metallic lustre, m. p. $60-61^\circ$.

R. V. S.

The Conjugation of the Products of Protein Hydrolysis to Colloidal Carbohydrates. H. FRIEDENTHAL (*Biochem. Zeitsch.*, 1913, 54, 174—181).—Attention is called to the fact that by the condensation of hydroxyl groups in polysaccharides of colloidal character with the amino-groups of amino-acids, it is theoretically possible to obtain derivatives which have the same empirical composition as proteins, and should yield the same reactions. Although it is not claimed that the majority of the proteins is constituted in this way, it is suggested that substances of this character may exist in the organism.
S. B. S.

Coagulation of Proteins by Ultra-violet Light. W. T. BOVIE (*Science*, 1913, 37, 24—25).—Exposure of certain proteins in quartz tubes to the rays of a quartz mercury-vapour lamp causes them to coagulate. Usually no coagulum forms in glass tubes, but dialysed crystallised egg-albumin is sensitive to longer wave-lengths than the fresh egg-white, since it coagulates in a glass tube. The coagulum has the same properties as that produced by heat without exposure to ultra-violet light.
E. F. A.

Temperature-coefficient of the Coagulum Caused by Ultra-violet Light. W. T. BOVIE (*Science*, 1913, 37, 373—375).—Two reactions are involved in the coagulation of proteins by light: the chemical change caused by the light, and the production of a visible coagulum. The light reaction, resembling other photochemical changes, has a very low temperature-coefficient. The chemical change producing the visible coagulum has a temperature-coefficient as high as two. Probably similar relations exist in other physiological processes which result from the action of light.
E. F. A.

The Precipitation of Colloids. II. KARL SPIRO (*Biochem. Zeitsch.*, 1913, 54, 155—158. Compare A., 1904, i, 124).—A table is given showing that salts, of which the hydrogen-ion concentration in solution is highest, have the greatest action in inhibiting the precipitation of proteins. The hydrogen-ion concentration of the mixtures of the salt and protein solutions is not the mean of the two, but in the case of the sodium, potassium, and lithium salts it is nearly the same as that of the original protein solutions, and in the case of the ammonium salts a little greater. The acetates form an exception, in that the hydrogen-ion concentration of the mixture of protein-salt solutions approaches very nearly the $[H^+]$ -concentration of the salt solution. The results seem to indicate the formation of a salt-protein compound, and the influence of salts on the precipitation of proteins is briefly discussed.
S. B. S.

The Content of the Blood-Plasma Proteins in Basic Constituents. KARL LOCK and KARL THOMAS (*Zeitsch. physiol. Chem.*, 1913, 87, 74—81).—The amounts of ammonia, arginine, histidine, and lysine in serum-albumin, serum-globulin, and fibrin were estimated and the table of results shows considerable discrepancies between

different preparations of the same protein, and according to the method used.

W. D. H.

The Soluble Protein Substances of Milk. LÉON LINDET (*Compt. rend.*, 1913, 157, 307—309).—The so-called albumin of milk possesses all the properties of caseinogen itself, with the exception of its rotatory power, where it has $[\alpha]_D - 30^\circ$ instead of -116° . The author suggests for it the name β -caseinogen, the α -caseinogen being the one, which is the chief constituent of the protein matter of milk. These two substances resemble one another closely in their solubility in milk serum, in their capillary adherence to the casein in suspension, in their precipitation by phenol, and in their partial coagulation at 75° .

W. G.

Influence of Calcium Chloride on the Curdling of Milk. LÉON LINDET (*Compt. rend.*, 1913, 157, 381—384. Compare preceding abstract).—Boiled milk is not clotted by rennet, but clots if a small amount of calcium chloride is added. This the author suggests is due to the interaction of the calcium chloride with the alkali phosphate and citrate in the milk serum, thus reducing the quantity of those, and rendering the two caseinogens less soluble. Further, the dicalcium phosphate by dissociation gives rise to phosphoric acid, which removes the calcium oxide from the caseinogens, rendering them still further insoluble.

W. G.

The Action of Rennin on Caseinogen. ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, 15, 231—236).—Calcium caseinogenate which is neutral to litmus is not curdled by rennin; but solutions which are acid and contain two equivalents of base for each molecule of caseinogen are curdled by rennin. Ammonium, sodium and potassium caseinogenates are not curdled by rennin. No other protein is formed except casein (2 molecules to one of caseinogen) during rennin curdling. Coagulation is the result of a change in solubility, and is the first stage in hydrolytic cleavage.

W. D. H.

Nucleohistone. I. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1913, 87, 207—213).—Nucleohistone prepared by the method given by Lilienfeld (A., 1894, ii, 146) had exactly the composition given previously. The whole of the nucleic acid present is proved to be true nucleic acid, no other substance containing phosphorus being present in nucleohistone.

E. F. A.

Processes Operative in Solutions, XXX, and Enzyme Action, XX. The Nature of Enzymes and of their Action as Hydrolytic Agents. E. FRANKLAND ARMSTRONG and HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1913, B, 86, 561—586).—A discussion of the problems of hydrolysis based on the experience gained in the course of two convergent series of enquiries.

The catalyst is defined as the agent which brings about the inclusion of the interacting substance in the circuit within which change takes place as soon as the circuit is established, the electrolyte being the

actual agent by which change is effected. Action between two non-electrolytes is impossible.

Enzymes are regarded as having a double function, namely, that of attracting or holding the hydrolyte and that of determining its hydrolysis. This twofold action is attributed to the presence in the enzyme of an acceptor together with an agent. The acceptor is a radicle very closely allied to a dominant group in the hydrolyte. The agent is an acid radicle in immediate or compatible proximity, so that a conducting path is formed between agent and acceptor by their association with the solvent. The efficiency of an enzyme depends also on its colloidal character. Each enzyme particle tends to absorb the hydrolyte, so that the solution at its surface is relatively concentrated; in addition it is hydrolated, the activity of the water molecules at the surface being greater than the average activity of the water. As a consequence the colloid surface remains highly charged with the hydrolyte probably up to the point at which the supply in the solution is exhausted.

The change is, therefore, not a simple mass action effect; in fact, in each successive interval of time the enzyme determines the hydrolysis of the same amount of hydrolyte. The observed departures from this rule are shown to be due to the influence of the products of change.

The relationship of the acceptor section of the enzyme to the hydrolyte is that of a superposable and, therefore, practically identical radicle.

The enzymes which hydrolyse the glucosides may be compounds of the glucoprotein class containing either α - or β -glucosidic radicles and therefore capable of hydrolysing either α - or β -glucosides, because their configuration harmonises with that of the one or of the other type of compound. Urease is an enzyme in which the urea residue in arginine is in suitable relationship with the carboxyl group. These conceptions are illustrated by photographs of solid models.

The resting enzyme is not an acid proper, but an internal salt of the glycine type. A substance of superior acidic power must be added to render the zymogen active. The action of acids and alkalis is considered from this point of view.

As the products of change accumulate in the solution, they affect the enzyme in various ways. The product immediately allied to the acceptor enters directly into competition with the hydrolyte. Other products act on the enzyme by neutralising it, by converting it into a derivative different in structure and no longer compatible with hydrolyte, or by changing the osmotic conditions in the solution, and altering the state of hydrolation at the colloid surface. These influences have been studied experimentally.

E. F. A.

The Velocity of the Appearance of Protective Enzymes after Repeated Introduction of the Foreign Substrate. I. EMIL ABDERHALDEN and ERWIN SCHIFF (*Zeitsch. physiol. Chem.*, 1913, 87, 225—230).—Whereas it takes some little time for the protective enzymes to appear on the first injection of a foreign peptone into the blood-serum, if a second injection is made, after the serum has become inactive again, the protective enzymes appear in a much

shorter time. The organism reacts much more rapidly to the second invasion. Experiments made on rabbits with silk peptone and gelatin peptone are described. The injection was preferably intravenous.

E. F. A.

Studies on the Specific Nature of the Intracellular Enzymes by means of the Optical Method. I. EMIL ABDERHALDEN and ANDOR FODOR (*Zeitsch. physiol. Chem.*, 1913, 87, 220—224).—The behaviour of the juices obtained from various macerated tissues after they had been completely deprived of blood was tested towards the peptones from each of the tissues. Whereas liver juice hydrolysed liver peptone, it had no action on kidney or thyroid peptone. Thyroid juice only attacked thyroid peptone. Kidney juice hydrolysed both kidney and liver peptones, and also, in one experiment out of three, it acted on thyroid peptone. The liver and thyroid cells contain enzymes adapted to their specific components only; the kidney cells have a wider function, and their enzymes are adapted to peptones from other sources.

E. F. A.

Enzymes of Fresh Foods. T. TADOKORO (*J. Coll. Agric. Sapporo, Japan*, 1913, 5, 57—72).—The fresh sap of Udo twigs, yams, cabbage and lettuce leaves, onions, ginger and radish roots of Japanese origin has been investigated for enzymes. Peptolytic action was only found in ginger and the onion. All the juices contained trypsin and a weak diastase, also oxydase and catalase, but they differed greatly in activity. Lipase was present only in the cabbage.

E. F. A.

Specific Nature of the Intracellular Enzymes by means of the Optical Method. II. EMIL ABDERHALDEN and ERWIN SCHIFF (*Zeitsch. physiol. Chem.*, 1913, 87, 231—232).—The enzymes in muscle juice (from the horse) hydrolyse muscle peptone, but not liver or brain peptone.

Testicle peptone is hydrolysed only by the enzymes in testicle and kidney juice. Brain peptone is hydrolysed only by brain and kidney juices.

E. F. A.

Some Conditions Affecting the Activity and Stability of Certain Ferments. JOHN H. LONG and WILLIAM A. JOHNSON (*J. Amer. Chem. Soc.*, 1913, 35, 1188—1201).—An extension of the earlier investigation on amylopsin (this vol., i, 919) to trypsin. Raw egg-albumin is found to be unsuited to the measurement of proteolytic action, and where egg-albumin is necessary, the authors make use of a Chinese dried albumin; but fibrin and casein are the best materials for comparative studies.

It is found that trypsin is not appreciably injured by the action of 0.3% hydrochloric acid for thirty minutes at 40°, for, although no digestion will occur in the presence of the acid, fibrin can be digested in considerable quantity after neutralisation.

Aqueous solutions of trypsin become weaker on long keeping at the ordinary temperature, the deterioration being more rapid the purer the product; in this respect it is more sensitive than pepsin. In the

presence of sodium carbonate between the concentrations 0.2% and 1% at 40°, the activity of trypsin in fibrin digestion is not affected.

D. F. T.

Purification of Invertase Preparations by Treatment with Acids. JAKOB MEISENHEIMER, STEFAN GAMBARJAN, and L. SEMPER (*Biochem. Zeitsch.*, 1913, 54, 108—121).—It is found that the content of invertase in a preparation can be increased by preliminary treatment of the expressed juices with acids. Not only acetic, but also hydrochloric, and more especially the dibasic sulphuric and oxalic acids effect this purpose. The addition of acids produces a precipitate of proteins, which carries down with it practically none of the ferment. The addition of too much acid acts deleteriously on the ferment, and for every preparation it is necessary, by means of preliminary experiments, to ascertain the amount of acid which yields the optimal result. For this purpose, the ferment is precipitated by means of acetone, and obtained in a dry form, and its reaction constant is determined polarimetrically with the employment of the equation $K = 1/4 \log a/a - x$. The above-stated facts are illustrated by numerous examples.

S. B. S.

Inhibition of Enzyme Action by Lime-softened Waters. OLAF BERGHEIM and PHILIP BOUVIER HAWK (*J. Amer. Chem. Soc.*, 1913, 35, 1049—1056).—It is found that lime-softened waters exert a pronounced inhibitory effect on the action of salivary and pancreatic amylases. Of the mineral constituents of the water, magnesium hydroxide exerts by far the greatest effect, whilst sodium carbonate and calcium carbonate have a less considerable effect. Investigation shows that the influence of the magnesium hydroxide is due to its existence in a colloidal form which adsorbs the enzyme. In contrast to the action of amylolytic ferments, peptic digestion is but little affected by magnesium hydroxide solution or by lime-softened water.

From the difference in effect of calcium carbonate solution on salivary amylase and pancreatic amylase, it appears that these enzymes are not identical.

D. F. T.

Action of Ammonia on Diastase Rendered Inactive by Heating. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, 86, 401—406).—Ammonia gas has the same effect on diastase whether it has been rendered inactive by heating or not. It cannot therefore have any action on those groupings in the molecule which are altered by heat, that is, on the groupings to which the activity of the enzyme is due.

E. F. A.

Action of Hydrogen Chloride and Ammonia on Diastase Rendered Inactive by Heating. XI. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, 87, 115—121).—Diastase which has been rendered inactive by heating, regains some feeble activity when treated first with dry hydrogen chloride and then with dry ammonia.

E. F. A.

The Enzymes of the Tobacco Plant. J. DU P. OOSTHUIZEN and OLIVER MARCH SHEDD (*J. Amer. Chem. Soc.*, 1913, 35, 1289—1309).—An investigation of the enzymes in two types of Kentucky tobacco, the White Burley variety of the Burley region, and the Yellow Pryor variety of Western Kentucky.

The results indicate the presence of appreciable amounts of invertase, diastase, emulsin, and reductases both in the seed and in the leaf at all stages of its growth and after curing. Small amounts of lipase, inulase, and a proteolytic enzyme also appear to be present. Oxydases were present in the green leaf, but the quantity decreased towards maturity, and was too small for definite detection in the cured leaf. Generally enzymes were found to be absent from the soil.

The probable rôles of the various enzymes are discussed.

D. F. T.

Enzymes in the Leaves of *Salix caprea*. IWAN BOLIN (*Zeitsch. physiol. Chem.*, 1913, 87, 182—187. Compare Armstrong, A., 1912, i, 816).—The leaves of *Salix caprea* may contain a salicase, an amygdalin-splitting and a glucoside-splitting enzyme. Salicase is specific for salicin, and has no action on β -methylglucoside. The enzyme acting on β -methylglucoside was present in the leaves in 1911, but absent from the leaves of the same tree in 1912.

E. F. A.

Enzyme Action. XXI. Lipase. III. HENRY E. ARMSTRONG and H. W. GOSNEY (*Proc. Roy. Soc.*, 1913, B, 86, 586—600. Compare A., 1906, i, 126; 1907, i, 103; Tanaka, A., 1910, i, 800).—Methods of preparing active lipase preparations from castor oil seeds in the form of a dry powder and of testing their hydrolytic activity are described. Dilute acetic acid is used to activate the zymogen, which is probably a salt. Lipase is very sensitive to the action of acids, and easily rendered inert by excess of acid. The inferiority as a hydrolyst of esters other than fats is due to the fact that the acids liberated from fats are scarcely soluble in water and very weak.

Lipase is specially fitted to hydrolyse the oily glycerides, and is not suited to act in aqueous solutions. Interaction takes place at and between surfaces separated only by a thin film of water. The interaction of enzyme and oil is inhibited by both the fatty acid and the glycerol, especially the former. As in other cases of enzyme action, the law of mass action does not apply, and the influence of the products of change and the destruction of the enzyme combine to cause departures from the simple law of enzyme action (compare this vol., i, 116).

Lipase is considered to contain a glycerol nucleus attached to a carboxylic centre in proximity to an acidic group, which can determine the hydrolysis of a fatty molecule that becomes attached to the glycerol acceptor.

E. F. A.

Some New Properties of Peroxydase. The Comparison of its Action with that of Nitrites. JULES WOLFF (*Ann. Inst. Pasteur*, 1913, 27, 554—567. Compare A., 1912, i, 928).—Plant sap is sufficiently acid to liberate nitrous acid from nitrites. The nitrous

acid thus set free is able to bring about oxidation phenomena similar to those caused by the combination of a peroxylase with hydrogen peroxide. Nitrites are decomposed by monopotassium phosphate.

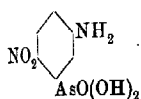
Peroxydase can be kept for some time in contact with ammonia without being changed. At first the oxidising activity diminishes somewhat, but then it increases, reaching the original value in four to five hours and attaining a maximum activity in forty hours, nearly double the original. This high activity persists for a time and then decreases slowly to the original value.

Orcinol absorbs oxygen from the air in presence of alkali hydroxides, carbonates, etc. The rate of absorption is greatly increased on adding a vegetable peroxydase—it may amount to five times the original value.

When the surface exposed to the air is large, orcinol absorbs oxygen, but does not form any quantity of coloured oxidation product (orcein). The addition of peroxydase increases the oxygen absorption, but not the amount of colour formed. On the contrary when the surface exposed to the air is small, only about one-seventh of the amount of oxygen is absorbed, but orcein is formed. Peroxydase accelerates the formation of the orcein and not the absorption of oxygen under these conditions.

E. F. A.

Preparation of a Nitro-3-aminophenyl-1-arsinic Acid. FARBERWERKE FORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 261643. Compare Berthelm, A., 1911, i, 1055).—When 3-oxalylaminophenyl-1-arsinic acid, $C_6H_4(AsO_3H_2) \cdot NH \cdot CO \cdot CO_2H$, needles, is dissolved in sulphuric acid, treated at 0–5° with 26% nitric acid, and the oxalyl group subsequently eliminated, it gives rise



to the hitherto undescribed 6-nitro-3-aminophenyl-1-arsinic acid, pale yellow needles; this when heated with concentrated alkalis yields 6-nitro-3-hydroxyphenylarsinic acid, whilst the mother liquor furnishes 2-nitro-3-aminophenylarsinic acid; and on reduction with sodium hyposulphite the corresponding diaminodihydroxyarsenobenzenes are obtained.

F. M. G. M.

Preparation of Neutral Derivatives of 3:3'-Diamino-4:4'-dihydroxyarsenobenzene, Soluble in Water. FARBERWERKE FORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 260235).—The preparation of compounds by the action of formaldehyde sulphonylate on 3:3'-diamino-4:4'-dihydroxyarsenobenzene have previously been described (A., 1912, i, 595), and the reaction has now been modified by dissolving the hydroxy-base in ethylene glycol before treating with formaldehyde sulphonylate and subsequently isolating the product by the addition of alcohol and ether.

F. M. G. M.

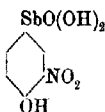
Preparation of Aromatic Stibinic Acids. CHEMISCHE FABRIK VON F. HEYDEN (D.R.-P. 261825. Compare this vol., i, 416).—*p*-Chlorophenylstibinic acid, a colourless powder, is obtained when a solution of *p*-chlorobenzenediazonium chloride is treated with antimony trichloride and the yellow precipitate of the additive compound (compare

May, T., 1912, 101, 1037) collected and decomposed with warm sodium hydroxide; it is purified by methods previously described (*loc. cit.*).

Phenylstibinic acid can also be obtained when aniline is diazotised in the presence of a mixture of antimony trichloride and hydrochloric acid, and the cooled solution slowly added to a solution of sodium hydroxide, when elimination of nitrogen occurs with the formation of the required product.

F. M. G. M.

Preparation of an Aromatic Nitrohydroxystibinic Acid.
CHEMISCHE FABRIK VON F. HEYDEN (D.R.-P. 259875. Compare A. 1886, 884; 1899, i, 209; 1910, i, 803; 1911, i, 594, 1056).—3-Nitro-



4-hydroxyphenylstibinic acid (annexed formula) is prepared by the following series of reactions. Anhydrous sodium *p*-acetylaminophenylstibinic acid (this vol., i, 416) dissolved in acetic acid (3 parts) is added drop by drop to 8 parts of concentrated sulphuric acid at a temperature below -2° ; above this, elimination of the acetyl group occurs; nitric acid (D 1.51) mixed with concentrated sulphuric acid at 0° is then added, and the mixture maintained at this temperature for several hours with continual agitation; on dilution, 3-nitro-4-acetylaminophenyl-1-stibinic acid is obtained as a yellowish-brown powder; this when heated with a solution of potassium hydroxide (D 1.30) loses ammonia and gives rise to the foregoing 3-nitro-4-hydroxyphenyl-1-stibinic acid, a brown powder, which when heated decomposes without fusion.

F. M. G. M.

Physiological Chemistry.

A Respiration Apparatus for Small Animals in which the Oxygen Consumption is Automatically Registered. L. S. FRIDERICIA (*Biochem. Zeitsch.*, 1913, 54, 92—167).—This apparatus combines the Haldane principle, according to which the animal with all excreta are weighed before and after the experiment, the water and carbon dioxide given out by the animal being collected in the ordinary absorption apparatus, with the Regnault-Reiset principle, modified more or less according to Benedict, in which the oxygen which is used up in respiration is automatically replaced from a gasometer, the amount added to the respiration apparatus being automatically registered. For these purposes a circulation is kept up through a closed system by means of a specially designed rotatory blower, which is figured in the text, and the air after leaving the cage containing the animal passes over weighed sulphuric acid and soda-lime tubes. In conjunction with this system is the oxygen holder, the lid of which is counterpoised by a

weight over a pulley, and the whole circuit is so arranged, by the interposition of wash-bottles serving as manometers, that it is constantly under atmospheric pressure. There is a double check, therefore, on the oxygen consumption, namely, the diminution of the oxygen in the gasometer, which is automatically registered, and the gain of weight in the animal holder and absorption apparatus. Both determinations yielded results concordant with one another.

S. B. S.

The Part Played by the Lungs in the Oxidative Processes of the Body. C. LOVATT EVANS and ERNEST H. STARLING (*J. Physiol.*, 1913, 46, 413—434).—The gaseous metabolism of the lung in the perfused heart-lung preparation is best measured in reference to the heart-weight as the lungs soon become œdematous. It is 1 c.c. of oxygen and 0.94 c.c. carbon dioxide per gram of heart per hour. The lungs do not exercise any general or specific activity in completing oxidations partly carried out in other tissues. W. D. H.

The Influence of the Carbon Dioxide Tension of the Blood on the Ventilation by the Lungs. OTTO PORGES and A. L. SAMPLE (*Biochem. Zeitsch.*, 1913, 54, 182—185).—In investigations on the influence of the acidity of the blood on the respiration, many authors have attempted to ascertain the stimulability of the breathing centre. Lindhard, more especially, has determined this factor, by allowing the subject of the research to inhale ordinary atmospheric air, and estimating the alveolar ventilation and carbon dioxide tension, and then determining the same factors after inhalation of air to which has been added varying amounts of carbon dioxide. Attention is now called to the fact that in these and similar experiments no account is taken of the fact that the effect on inhaling increased amounts of carbon dioxide will vary according to the pre-existing stimulus. As this pre-existing stimulus depends on the acidity of the blood, it is necessary to take into account, not only the carbon dioxide tension, but also the amount of non-volatile acids, which, according to Porges and his co-workers, are present accompanied by a diminished carbon dioxide tension in acidosis. The influence of the amounts of acid on the action of lungs is illustrated by some experiments on a pregnant patient, and patients with diabetes, and the conclusion is drawn that the method employed by Lindhard and others is not adapted to the determination of the true stimulability of the respiratory centre.

S. B. S.

Influence of Alcohol on the Respiratory Exchange During Rest and During Muscular Exercise. C. J. C. VAN HOOGENHUYZE and J. NIEUWENHUYSE (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 164—172).—The authors have subjected themselves to experiments on the influence of alcohol on the respiratory exchange. While resting, they measured the oxygen-intake and carbon dioxide-output by means of the Zuntz-Geppert apparatus, and found that the respiratory quotient, CO_2/O_2 , remained lower for a few hours after

the consumption of alcohol. The experiments involving muscular exercise were performed on a bicycle with adjustable and registrable resistance. The brake-band was tightened until the subject was fatigued, and then, whilst he was pedalling against a constant resistance, without or after a dose of 60 c.c. of 96% alcohol, the respiratory exchange was examined as above. The experiments were performed at 8–15° and at 28°. The respiratory quotient was again found to be lowered for a time after the consumption of alcohol, even at the higher temperature, at which muscular work was less economically performed. Alcohol, therefore, can produce energy for muscular exercise, and this is more economically performed for an hour or two after taking the stimulant. This favourable influence, however, gradually decreases, and tends towards the opposite in time.

J. C. W.

The Influence of Muscular Rigidity on the Oxygen-intake in Decerebrate Cats. HERBERT E. ROAF (*Quart. J. expt. Physiol.*, 1913, 6, 393–402).—During decerebrate rigidity the oxygen intake is only slightly greater than when the muscles are flaccid.

W. D. H.

Rate of Reproduction of the Blood Constituents in an Immunised Horse After a Large Bleeding. R. A. O'BRIEN (*J. Path. Bact.*, 1913, 18, 89–98).—After the withdrawal of ten litres of blood from an immunised horse, the fluid first appearing in the circulatory system contains an amount of protein far above the normal; hæmolyisin and diphtheria antitoxin are reproduced at different rates, and the rate of reproduction of the various blood-proteins is probably associated therewith. Details regarding salts and corpuscles are also given.

W. D. H.

The Effect of Certain Drugs, Toxic Substances, and Micro-organisms on the Fragility of the Red Corpuscles of Man and Animals. W. W. C. TOPLEY (*J. Hygiene*, 1913, 13, 191–236).—Arsenious acid and atoxyl in toxic doses increase the fragility of red corpuscles *in vivo*. Bile and bile salts cause no change. Various pathogenic hæmolytic micro-organisms cause a rise in fragility, so also do specific hæmolytic sera; the amboceptor alone does not. Experiments *in vitro* were not satisfactory, but, so far as they went, the results confirmed the findings *in vivo*.

W. D. H.

The Formation of Indophenol at the Nuclear and Plasma Membranes of Frog's Blood Corpuscles, and its Acceleration by Induction Shocks. RALPH S. LILLIE (*J. Biol. Chem.*, 1913, 15, 237–247).—The formation of indophenol by the intracellular oxidation of α -naphthol and dimethyl-*p*-phenylenediamine takes place most rapidly in the neighbourhood of the nuclear and plasma membranes. This is accelerated by passing induction shocks through the suspension of blood corpuscles.

W. D. H.

Rapid Method of Preparing Thrombin. WILLIAM H. HOWELL (*Amer. J. Physiol.*, 1913, 32, 264–265).—Pig's fibrin is well washed,

and then extracted with 8% solution of sodium chloride; the extract is heated with an equal volume of acetone; the bulky precipitate of protein contains thrombin; this is filtered off and rapidly dried, then extracted with water, and filtered; the filtrate contains the thrombin, traces of salt, and a heat-coagulable protein; the latter is removed by shaking with chloroform, and the final fluid is evaporated to dryness in a current of cold air. The dried material can be left indefinitely in a desiccator. It is easily and completely soluble in water.

W. D. H.

The Relation of Metathrombin to Thrombin. F. W. WEYMOUTH (*Amer. J. Physiol.*, 1913, 32, 266—285).—The thrombin content of serum is determined by its clotting power on solutions of fibrinogen, and the metathrombin content by the clotting power after activation by alkali and subsequent neutralisation. In dog's serum the activity of both disappears after three to four days; five to eighteen days later there is almost complete return, and then it disappears completely. If kept sterile the initial loss of power is slower, and there is no reappearance of activity. Bacterial growth is responsible for both phases. Thrombin prepared by Howell's method retains its power for long periods (at least eighteen days); its power is destroyed by a substance in serum and in oxalate plasma, which is antithrombin. After the action of antithrombin the presence of metathrombin can still be shown in certain cases. Metathrombin is regarded as a thrombin-antithrombin compound; it is absent in oxalate and fluoride plasma.

W. D. H.

The Nitrogen of Blood-serum Freed from Protein. RUDOLF PHILIPP (*Zeitsch. physiol. Chem.*, 1913, 86, 494—502).—The residual nitrogen after serum has been freed from protein by heat-coagulation is about twice as great as when phosphotungstic acid, uranyl acetate, or ferrum oxydatum dialysatum are employed. The two last-named reagents entirely free the serum from protein. In cases of uræmia the residual nitrogen is increased.

W. D. H.

Alterations Produced in Complement-containing Sera by the Introduction of "Lecithin." JOHN CRUICKSHANK and THOMAS J. MACKIE (*J. Path. Bact.*, 1913, 18, 99—113).—"Lecithins" differ markedly with regard to their power to produce the alterations in complement activity, hæmolysis, etc., with which the paper deals. A large number of preparations are quite inefficient.

W. D. H.

Fibrin in Sol and Gel State. The Blood-coagulation Problem. EBEL HEKMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 172—185).—The author has investigated the relation between fibrinogen and fibrin. Pure fibrin, free from blood corpuscles, was found to dissolve quite readily in very dilute sodium hydroxide or sodium carbonate, but a fibrous coagulum could be reproduced by the cautious addition of dilute acids, such as phosphoric or carbonic, or by sodium dihydrogen phosphate or calcium chloride.

Fibrin also dissolved in a slight excess of acid, but could be reprecipitated on neutralisation. Coagulation was also effected in solutions which had been boiled, from which the conclusion is drawn that ferments play no part in the process. Fibrin is therefore a reversible gel.

Further experiments showed that centrifugated, fluid plasma, or ascites fluid (that is, a natural fibrinogen solution), like alkaline fibrin solutions, could be coagulated by traces of acids. Moreover, alkaline fibrin solutions could be coagulated by serums or organic extracts which are known to coagulate fibrinogen, and also, like fluid plasma or ascites fluid, by means of saturated solutions of sodium chloride or fluoride. A great similarity was thus established between fibrinogen as found in blood and body fluids, and a solution of fibrin in very dilute alkali.

Dried fibrils, the single threads of fibrin, swell out again very quickly in alkaline solutions, and, if the volume of liquid is small, raw fibrin will imbibe the whole of it and become jelly-like. A swollen fibril, however, contracts to its original size in dilute acids, 1% calcium chloride or any saturated salt solution, or even in excess of water. The swelling process is therefore of a superficial kind, and it is assumed that it consists in the formation of an alkali adsorption-compound, which eventually, by the continuation of the imbibition, passes into colloidal solution. Fibrinogen is thus considered to be an alkali-hydrosol of fibrin, and its conversion into the gel, fibrin, and therefore the coagulation of blood, is merely due to the withdrawal of hydroxyl ions from the adsorption compound by means of one or other of the factors mentioned above.

J. C. W.

The Inhibition of Hæmolysis by Cholesterol and Oxysterol. E. SCHREIBER and LÉNARD (*Biochem. Zeitsch.*, 1913, 54, 291—296).—A method is described for preparing oxysterol from cholesterol, and of obtaining emulsions of the same. Although, by itself, the former substance has a much weaker power of inhibiting hæmolysis than cholesterol, it increases this power of the latter substance when added to it in quite small quantities. Oxysterol acts also more weakly than cholesterol in inhibiting hæmolysis by cobra poison.

S. B. S.

The Influence of Nutrition on the Gaseous Metabolism of Cold-blooded Animals. BERNHARD ELSAS (*Zeitsch. Biol.*, 1913, 62, 1—31).—The experiments were made on groups of frogs in a modified Regnault-Reiset apparatus. The inanition metabolism is first found; but as this is influenced by the temperature, all the observations must be carried out at a constant temperature. Food may then be given in amounts equivalent to the inanition metabolism (isopeinic), or the quantities may be below or above this (hypo- and hyper-peinic respectively). Iso- and hyper-peinic administration of dextrose increases the metabolism by from 6 to 20%. Isopeinic feeding with fat does not raise the metabolism. The increase of metabolism after isopeinic feeding on protein is

very pronounced, 17—40%. These results are compared with some previously published by Weiss. The observations lend no support to the view that the increase of activity is due to alimentary work, but confirm Rubner's views on the specific dynamic values of foods.

W. D. H.

Metabolism of Ammonium Salts. I. The Estimation of Ingested Ammonium Salts in the Dog on an Adequate Mixed Diet. FRANK P. UNDERHILL (*J. Biol. Chem.*, 1913, 15, 321—335).—Ammonium salts of organic acids were given to dogs on a fixed diet, but failed to increase the ammonia nitrogen of the urine. Ammonium salts and inorganic acids caused a varying degree of increase in the ammonia nitrogen of the urine. The experiments afford no adequate explanation for the temporary retention of the ammonium salts. All the inorganic ammonium salts used, and some of the organic salts, cause a distinct excess of total urinary nitrogen, and they apparently stimulate nitrogenous katabolism. Sodium chloride under the same conditions lowers the output of urinary ammonia nitrogen.

W. D. H.

Metabolism of Ammonium Salts. II. Elimination of Ammonium Salts During a Period of Prolonged Inanition. FRANK P. UNDERHILL (*J. Biol. Chem.*, 1913, 15, 337—339).—During inanition in the dog, ingestion of ammonium carbonate fails to produce an increase of urinary ammonia nitrogen. Ammonium chloride causes, however, a marked increase, and also an increase in total nitrogen. At this stage a second ingestion of ammonium carbonate may also bring about an increase of total urinary nitrogen.

W. D. H.

Metabolism of Ammonium Salts. III. The Utilisation of Ammonium Salts with a Non-nitrogenous Diet. FRANK P. UNDERHILL and SAMUEL GOLDSCHMIDT (*J. Biol. Chem.*, 1913, 15, 341—355).—Ammonium chloride added to a non-nitrogenous diet caused no retention of nitrogen, as Grafe states. It exercises a toxic action, and increases the output of urinary ammonia. Ammonium acetate and citrate decrease the nitrogen loss, and lead to retention of nitrogen. The ability of the body to deal with the organic and inorganic salts of ammonium is radically different.

W. D. H.

Excretion of Creatine. R. A. KRAUSE (*Quart. J. expt. Physiol.*, 1913, 7, 87—101).—The metabolism of children differs from that of the adult. In boys, creatinuria occurs until the age of five or six; in girls it persists longer, and may last until the intermittent creatinuria occurs which characterises the female sexual cycle. The power to assimilate creatine given with the food is much weaker in children than in the adult. The excretion or non-excretion of creatine depends on the balance between formation and destruction, two processes which are always at work. This view will render it necessary to revise current theories on creatinuria as a pathological condition.

W. D. H.

Nitrogen Retention in Feeding on Urea. EDUARD GRAFE (*Zeitsch. physiol. Chem.*, 1913, 86, 347—355).—These experiments are given to support the author's contention (compare A., 1912, ii, 659; 1913, i, 216) that urea in the food leads to retention of nitrogen. The experiments lasted over a long period. W. D. H.

The Relation of Growth to the Chemical Constituents of the Diet. THOMAS B. OSBORNE, LAFAYETTE B. MENDELL, EDNA L. FERRY and ALFRED J. WAKEMANN (*J. Biol. Chem.*, 1913, 15, 311—326).—It has been previously shown that growth and maintenance are different things. The best food to promote growth is milk, even if only small quantities are occasionally given, mixed with an artificial diet of protein, fat, carbohydrates, and salts. Protein-free milk is not adequate for growth, but the addition of butter to the protein-free milk restores growth. Evidently some substance is removed from the protein-free milk which is essential, and this is present mixed with the butter-fats. What the substance is, is as yet unknown. W. D. H.

Sugar Absorption. KORNÉL VON KÖRÖSY (*Zeitsch. physiol. Chem.*, 1913, 86, 356—367).—By interference with the circulation through the intestines, lungs, and heart, absorbed sugar does not occur as such in the blood. The absorption of sugar is not a simple process, and the effect of internal secretions, such as that of the adrenal gland, has to be taken into account. Phosphates may also play an important rôle in sugar absorption, as they do in alcoholic fermentation. W. D. H.

The Distribution of Creatine in the Animal Organism J. C. BEKER (*Zeitsch. physiol. Chem.*, 1913, 87, 21—37).—A large number of organs and tissues in different animals were found to contain creatine in amounts which are greater than that in the blood. These results are given in tables. Experiments are also given which confirm the view that the liver is able to convert creatine into creatinine. W. D. H.

The Lecithin Content of Different Tissues. JOHN CRICKSHANK (*J. Path. Bact.*, 1913, 134—136).—The amount of lecithin in various tissues was estimated by the author's method. In 100 grams of moist tissue, ox red corpuscles yielded 2.5, sheep's liver 1.6, human brain 0.6, ox pancreas 0.68, testicles 0.62 gram, and other tissues amounts varying from 0.14 to 0.48 gram. W. D. H.

Gases Evolved During the Autolysis of Some Organs and Tissues. FILIPPO TRAIETTA-MUSCA (*Gazzetta*, 1913, 43, ii, 144—148).—The liver, kidney, brain, and suprarenal capsules yield carbon dioxide, nitrogen, and hydrogen; the intestine evolves carbon monoxide and oxygen in addition to these gases, whilst the pancreas, spleen, lungs, and heart yield only nitrogen. R. V. S.

Calcium and Magnesium in the Brain Under Different Physiological and Pharmacological Conditions. IVO NOVI (*Eighth Inter. Cong. App. Chem.*, 1912, 19, 261).—The proportion of

calcium in the brain of the dog varies from 0.0143 to 0.031, and that of magnesium from 0.0143 to 0.0167% of the fresh material. Age has a marked influence on the calcium-content of the brain. With dogs this content is at its maximum before and just after birth, the minimum is reached prior to weaning, and in old age the initial value is again attained; a similar course is followed in the case of the human brain. With guinea-pigs, the proportion of calcium is minimal in the fœtus, becomes almost doubled a few days after birth, and continues to increase for a month; subsequently it remains constant until old age is reached, when it again increases, sometimes as much as tenfold. Introduction, either subcutaneously or into the stomach, veins, or carotids, of sodium chloride in isotonic or hypertonic solution results in the diminution of the calcium-content of the brain, in some cases by one-half. The proportion of magnesium in the brain remains constant at all ages and under all the experimental conditions employed.

T. H. P.

Cerebrosides of Brain Tissue. PHOEBUS A. LEVENE (*J. Biol. Chem.*, 1913, 15, 359—364).—The conclusion that the cerebrosides are optically different isomerides is confirmed by further work, but more data are still wanting to render this certain. W. D. H.

Autolysis of, and Presence of, Proteolytic Ferments in the Brain of the Calf. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, 43, ii, 133—143).—When the brain of the calf is subjected to autolysis (incubation with water in presence of chloroform for a month), lysine, choline, xanthine, and adenine can be subsequently obtained from it. This indicates the presence in the brain of ferments capable of attacking albumin, nucleins, and lecithin. R. V. S.

The Effect of Alcohol on the Excitation, Conduction, and Recovery Processes in Nerves. KEITH LUCAS (*J. Physiol.*, 1913, 46, 470—505).—After exposure to 5% alcohol, a nerve recovers its properties when replaced in Ringer's solution. The impairment of conduction in the nerve produced by alcohol, and the increase in threshold current strength follow a parallel course. The rate of conduction is much slowed, however, at a stage when the rate of recovery is not slowed. This suggests that the recovery process, which is responsible for the refractory period, is a process different from the disturbance which is the basis of propagation of the nervous impulse.

W. D. H.

The Influence of Anoxybiosis on the Disappearance of Glycogen from the Autonomously Organs of the Frog. ERNST J. LESSER (*Biochem. Zeitsch.*, 1913, 54, 236—251).—As autonomous organs are designated those tissues, such as liver and muscles, in which action takes place when they are separated from the nervous systems, and the hormones contained in the blood supply. The author has already shown that the rate of glycogen disappearance from the liver after removal from the animal is greater in summer

frogs than in winter frogs, and he now compares this rate when the organs are well supplied with oxygen (oxybiosis) and when they are kept in a current of nitrogen (anoxybiosis). These experiments were of interest, as it has been found that under the influence of anoxybiosis of the whole animal the rate of glycogen disappearance could be increased, and it was thought possible that by this means the behaviour of the livers from winter frogs could be made to approximate to that of summer frogs. It was found that in the months of the year in which the glycogen of the liver is stable, the rate of disappearance is not influenced by anoxybiosis, whereas in the months when the glycogen is labile, anoxybiosis increases the rate. The experiments were carried out at the temperature of 22—24°, and did not extend beyond five hours. Similar results were obtained with muscular tissues.

S. B. S.

Chemical and Bio-chemical Properties of the Lipoids Extracted from Pig's Liver and Egg-yolk. FREDERICK P. WILSON (*J. Path. Bact.*, 1913, 18, 60—63).—The lipoids extracted from pig's liver and from egg-yolk differ greatly in their chemical (iodine value, etc.) and biochemical (anti-complementary, hemolytic powers, etc.) properties.

W. D. H.

The Thyroid Gland. XI. WALTER EDMUNDS (*J. Path. Bact.*, 1913, 18, 52—59).—The thyroid gland in dogs hinders the assimilation of sugar; the parathyroid glands favour it.

W. D. H.

Carbohydrate Metabolism in its Relation to the Thyroid Gland. The Effect of Thyroid Feeding on the Glycogen-content of the Liver and on the Nitrogen Distribution in the Urine. W. CRAMER and R. A. KRAUSE (*Proc. Roy. Soc.*, 1913, B, 86, 550—560).—When rats or cats are fed on a carbohydrate-rich diet plus small amounts of fresh thyroid gland for two or three days, the liver only contains traces of glycogen. This is due to an inhibition of the glycogenic function of the liver, and not to increased utilisation of carbohydrates. There is no glycosuria. The distribution of the nitrogenous constituents in the urine is similar to that observed after withdrawal of carbohydrates from the diet.

W. D. H.

Changes in the Metabolism of Animals After Extirpation of the Thyroids and Parathyroids. J. GREENWALD (*Biochem. Zeitsch.*, 1913, 54, 159—160).—The author controverts the statement of Paladino (this vol. i, 675) that there is an increased phosphorus output after extirpation of the thyroids. He contends that there is rather a diminution, and the discrepancy between Paladino's results and those of other authors is due to the fact that the former did not investigate the metabolism immediately after the operation, but only after a prolonged period at the onset of tetany, which, it is admitted, may produce increased phosphorus output.

S. B. S.

The Enzymes of the Pituitary Body. LUCIE BUETOW (*Biochem. Zeitsch.*, 1913, 54, 40—52).—The following ferments were found to be present: Catalase, diastase, pepsin, trypsin, peroxydase, tributyrinase, and urease. The following enzymes could not be detected: Invertase, lactase, a glycolytic ferment, and deamidase. S. B. S.

The Chemistry of the Mammary Gland. J. ARGYLL CAMPBELL (*Quart. J. expt. Physiol.*, 1913, 7, 53—56).—Considerable differences exist in the mammary gland of different animals, and even between different parts of the gland in the same animal. Lactose is found only when the gland contains milk, and the amount present is thus a measure of the quantity of milk in the gland. The fat, on the other hand, is present, not only in milk, but in the secreting cells, and in the adipose tissue between the alveoli. W. D. H.

The Phosphatides of Human Placenta. III. C. SAKAKI (*Biochem. Zeitsch.*, 1913, 54, 1—4).—From the alcohol-ether obtained in the purification of the so-called jecorin by Drechsel's method, a precipitate was obtained on addition of alcoholic cadmium chloride, part of which was soluble in ether and the other part insoluble. Both these products were analysed, but the results do not accord with any definite chemical formula. S. B. S.

The Distribution of Phosphorus in the Placenta. C. SAKAKI (*Biochem. Zeitsch.*, 1913, 54, 5—10).—From the determination of the phosphorus soluble in organic solvents (light petroleum or benzene) the amount of lecithin was calculated as 6.8% of the dried substance. S. B. S.

The Absorption of Water by the Skin of the Frog. S. S. MAXWELL (*Amer. J. Physiol.*, 1913, 32, 286—294).—An empty frog's skin immersed in water takes up an enormous amount; this depends on the permeability of the skin to water, and its relative impermeability to salts. The assumption of "vital activity" in this process is regarded as unnecessary. W. D. H.

The Absolute Mechanical Efficiency of the Contraction of an Isolated Muscle. ARCHIBALD V. HILL (*J. Physiol.*, 1913, 46, 435—469).—Fick's results on the mechanical efficiency of muscular contraction are inaccurate; for instance, they do not take into account the heat-production which occurs in the period of recovery. The subject was re-investigated by the author's new methods; his apparatus, however, requires calibration for each experiment and each muscle used. In the sartorius, the initial process of contraction consists mainly of the liberation of free potential energy, which is manifested as tension energy in the excited muscle; this can be used indifferently for the production of work or of heat; the efficiency of the whole process may be almost as high as 50%. The chemical substance possessing the free energy is the lactic acid precursor. W. D. H.

Extractives of Muscle. XV. Presence of Carnosine, Methylguanidine, and Carnitine in Horse Flesh. J. SMORODINZKY (*Zeitsch. physiol. Chem.*, 1913, 87, 12—20).—Horse flesh is shown to contain about 0.58 gram of creatine, 0.08 gram of purine substances, 1.82 gram of carnosine, 0.18 gram of carnitine, and from 0.11 to 0.83 gram of methylguanidine per kilogram of fresh muscle. These proportions are those observed in the muscles of other animals. E. F. A.

The Influence of Starvation on the Creatine Content of Muscle. VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1913, 15, 283—304).—The creatine of rabbit's muscle is relatively increased in the early part of starvation, but decreased at the close, owing to its loss by the urine. That creatine and creatinine are independent in metabolism is dissented from; the old view that the creatinine is derived from muscular creatine is favoured, though the proof is not yet complete. W. D. H.

Influence of Carbohydrate Feeding on the Creatine Content of Muscle. VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1913, 15, 305—310).—The effect of carbohydrate feeding on the creatine of rabbit's muscles is similar to that seen in starvation. The decreased elimination of creatine under these conditions is primarily dependent on the sparing action of carbohydrate on the muscle proteins. W. D. H.

The Derivatives of Ethyl Alcohol Contained in Muscle. ALONZO L. TAYLOR (*J. Biol. Chem.*, 1913, 15, 217—220).—In dogs which had been without food for one day, and in which the entire alimentary canal had been extirpated, the muscles still yielded alcohol in small amounts. It could not have been derived from food, and the theory is advanced that alcohol is an intermediate stage in the metabolism of dextrose. W. D. H.

Chemical and Physico-chemical Properties of Liquids Expressed from Striated and Plain Muscle. II. Amount of Protein in the Juice and Relations between the Granules (Myosin) Suspended and the Myoprotein Dissolved. FILIPPO BOTTAZZI and G. QUAGLIARIELLO (*Atti R. Accad. Lincei.*, 1913, [v], 22, ii, 52—59. Compare Bottazzi, A, 1912, ii, 1192).—The granular substance amounts to 33—61% of the total protein of the juice. The total protein amounts to 5.32—9.54%. Data regarding the yield, density, viscosity, total nitrogen, and ash of the juice obtained in different experiments and with muscle from different animals are also recorded. R. V. S.

Presence of Succinic Acid in Meat Extract and in Fresh Meats. HANS EINBECK (*Zeitsch. physiol. Chem.*, 1913, 87, 145—158).—Succinic acid in some quantity is obtained, both from Liebig's meat extract and from fresh ox and dog flesh. It is present in the carniferrin fraction, and particularly in the mother liquors from

this. It is not derived from the decomposition of Siegfried's phosphorcarbic acid.
E. F. A.

Does Milk Contain Phosphatides? VLADIMIR NJEGORAN (*Biochem. Zeitsch.*, 1913, 54, 78—82).—Milk was treated with anhydrous sodium sulphate, and the mixture was kept in a vacuum until free from water. The residual powder was then extracted with various organic solvents. No phosphorus could be detected in these solutions, and the author draws the conclusion that phosphatides are not present in milk.
S. B. S.

The Effect of Pituitary Extract on the Secretion of Milk. JOHN HAMMOND (*Quart. J. expt. Physiol.*, 1913, 6, 311—338).—Injection of pituitary extract produces an immediate action on the flow of milk, which is followed by a period of decreased flow. The effect, however, is not muscular, nor is it effected through the rise of blood-pressure. Microscopic evidence points to a direct action on the epithelium cells which set free the milk constituents. The milk formed is rich in fat. The daily yield of milk is only slightly increased as the result of the injection.
W. D. H.

Hydrocephalus Fluid. E. SIEBURG (*Zeitsch. physiol. Chem.*, 1913, 86, 503—510).—An analysis of fluid from a case of hydrocephalus is given. The noteworthy points are: (1) the absence of protein; a faint reaction with Millon's reagent indicates the presence of certain hydrolytic products of protein; and (2) the presence of certain enzymes, namely, diastase, invertase, lipase, and enzymes capable of splitting glucosides and esters.
W. D. H.

The Nature of the Depressor Substance in Dog's Urine and Tissues. ALONZO A. TAYLOR and RICHARD M. PEARCE (*J. Biol. Chem.*, 1913, 15, 213—216).—Attempts to isolate the substance failed.
W. D. H.

The Excretion of Formic Acid in Human Urine Under Normal and Pathological Conditions. RUDOLF STRISOWER (*Biochem. Zeitsch.*, 1913, 54, 189—211).—The formic acid was estimated by distilling urine acidified with phosphoric acid under diminished pressure, collecting the distillate in excess of alkali, and determining the acid in this distillate after concentration by heating with mercuric chloride in the presence of sodium acetate. The mercurous chloride produced by the reduction was weighed. The yield of formic acid thus found is about 90% of the theoretical. Formic acid is found under normal conditions in the urine to the extent of about 13.5 milligrams daily; and the amount is not increased by moderate muscular activity. It does not appear to be influenced by the character of the diet. In many diseases the amount excreted is normal, as in compensated heart affections, carcinoma, gastric ulcer, colicithiasis, constipation, and various febrile conditions. It is increased, however, in uncompensated heart affections, in asphyxia due to work in heart affections in man,

and in animals. It is also increased in diabetes as the result of changes in the fat metabolism. In a single case investigated of muscular dystrophy there was also found an increased output of the acid, due apparently to changes in the muscular metabolism. Reasons are given for supposing that formic acid is a metabolism product of fats, carbohydrates, and proteins. S. B. S.

Excretion of Formic Acid in Disease. I. GREENWALD and N. W. JANNEY (*Zeitsch. physiol. Chem.*, 1913, **86**, 511—512).—By the use of the method of Dakin, Janney, and Wakeman, it is shown that the excretion of formic acid in the urine is increased in pneumonia, especially during the stage of resolution. Figures are also given in isolated cases of other diseases, but no generalisations are possible from these. W. D. H.

Substances in Urine Giving Rise to Indigotin. I. ROBERT V. STANFORD (*Zeitsch. physiol. Chem.*, 1913, **87**, 188—206).—The substances in human urine which give rise to indigotin are very unstable. Their amount has greatly diminished in one to three hours, and they have disappeared in three to six hours. The cause of the decomposition is not understood; it is perhaps due to autoxidation. The indigotin-forming substances were obtained by salting-out and extraction with a mixture of ether and alcohol. Even under these conditions they decompose too rapidly for their isolation to be effected. It is considered improbable that they are identical with potassium indoxylsulphate. E. F. A.

Excretion of Morphine in the Urine. WILHELM RITTER VON KAUFMANN-ASSER (*Biochem. Zeitsch.*, 1913, **54**, 161—173).—The author finds that neither the biological method of Hermann and Straub (action on white mice) nor the chemical method described by van Ryn are suitable for the quantitative estimation of morphine in the urine. He describes a method devised by himself, in which the morphine is finally extracted with chloroform, and estimated by means of iodococain. By this method it is found that larger quantities of the alkaloid are excreted by the kidneys than was formerly supposed, the amount eliminated by this channel reaching 39% during a course of constant administration of the drug. Seventy-two hours after the last injection in this series of experiments sufficient alkaloid could be found in the liver, kidneys, and stomach for quantitative estimation. S. B. S.

The Antagonism Between Adrenaline and Anaesthetics on the Heart. JAMES A. GUNN (*Quart. J. expt. Physiol.*, 1913, **7**, 75—86).—Using the perfusion method on the heart of cat or rabbit it was found that adrenaline can antagonise a concentration of chloroform which enfeebles the beat, but not such a concentration as arrests it. In the case of chloral the antagonism of adrenaline is greater, and the latter drug will set a heart going which is completely arrested by chloral. Adrenaline is also antagonistic to many other substances which weaken cardiac activity. The

rhythmic contractions which adrenaline arouses in a quiescent heart are independent of intrinsic motor ganglia. W. D. H.

Pharmacological Testing of Sulphuric Acid. Esters of Atropine and Scopolamine. PAUL TRENDLENBURG (*Arch. expt. Path. Pharm.*, 1913, 73, 118—138).—By the esterification of the alcoholic hydroxyl of alkaloids of the atropine group with sulphuric acid, the intramolecular salt formation with the nitrogen of the tropine or scopolamine causes a marked weakening of their affinity for the endings of the vagus nerve. In most cases the stimulating action on the nervous system is increased. The toxicity is not altered as a rule. The esters of the atropine group stimulate the respiratory centre very strongly; this may be useful therapeutically. The scopolamine ester does not possess this property. W. D. H.

Creatine Formation in the Animal Kingdom. Creatine Formation from Betaine and Choline. OTTO RIESER (*Zeitsch. physiol. Chem.*, 1913, 86, 415—453).—This paper contains a very useful résumé of recent work on the subject. The experiments recorded deal with the effect of the administration of betaine and choline (by mouth or hypodermically) on the amount of creatine in the muscles, and creatinine in the urine. In some cases the material was mixed with surviving muscle. Although in a certain number of cases creatine or creatinine, as the case may be, was increased, the conclusion is drawn that there is no certain proof that betaine or choline leads to creatine formation. W. D. H.

The Fate of Cocaine and Ecgonine in the Organism. SULEIMAN RIFÄTWACHDANI (*Biochem. Zeitsch.*, 1913, 54, 83—91).—Cocaine is excreted, after administration to rabbits, in the urine, in amounts which can be quantitatively estimated. For this purpose the urine is extracted by benzene or ether, and the amount of alkaloid thus obtained is estimated by Gordin's method. By long-continued administration of the drug, the amount excreted each day in the urine gradually increases. No destruction of cocaine, when kept in contact with living tissue, could be detected. Ecgonine is also excreted in the urine; for the purposes of detection the urine was evaporated to dryness and treated with methyl alcohol and hydrochloric acid; the alkaloid after conversion into its methyl ester can be extracted by ether. S. B. S.

The Influence of Lecithin on the Action of Drugs. DAVID M. LAVROV (*Biochem. Zeitsch.*, 1913, 54, 16—26 Compare Han-clundt, his vol., i, 196).—A summary is given of earlier experiments on the combined action of lecithin and various drugs on frogs, in which it is shown that within certain limits the lecithin diminishes the action of the drug, whereas within higher limits it increases it. In the cases of phosphorus and phenol poisoning, an increase only of the toxic effect was observed. In doses of 0.0015 to 0.003 gram lecithin markedly increases the toxic action of ricin on frogs. Doses of other magnitudes cause a two-fold action. During the first ten

or eleven days they increase the toxic action, but afterwards the ricin effects begin to weaken. The general condition of the animals employed is not without effect. S. B. S.

Is the Pressor Effect of Pituitrin Due to Adrenal Stimulation? R. G. HOSKINS and CLAYTON MCPEEK (*Amer. J. Physiol.*, 1913, **32**, 241—244).—The experiments recorded show that the answer to the question is in the negative. W. D. H.

Pharmacological Notice Concerning Two New Derivatives of Santonin, α - and β -Santonan (α - and β -Tetrahydrosantonin). E. SIEBURG (*Chem. Zeit.*, 1913, **37**, 945—946).—Pharmacological experiments with α - and β -sodium tetrahydrosantonate (Wienhaus and von Oettingen, this vol., i, 474) show that they are not cramp poisons, neither do they act as vermicides. The reduction of the ethylene linking in santonin thus destroys its specific properties. T. S. P.

***p*-Hydroxy- β phenylethylamine, the Poison in the Salivary Gland of Cephalopods.** MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1913, **87**, 51—58).—*p*-Hydroxy- β -phenylethylamine is shown to be the only poisonous constituent of the saliva of the octopus. This base, which had previously been obtained by Barger and Dale from ergot (*A.*, 1909, ii, 689), is thus, like adrenaline, the product of metabolism in a gland. E. F. A.

Chemistry of Vegetable Physiology and Agriculture.

The Resistance of Spores to Heating in Anhydrous Fluids such as Glycerol and Similar Substances. HOWARD BULLOCK (*J. Hygiene*, 1913, **13**, 168—177).—The method at present in use for the sterilisation of glycerol or oil are quite inadequate; the heating of these fluids has no greater effect than the same temperature in the air. To sterilise these fluids, a temperature of 170° for half an hour or 180° for ten to fifteen minutes is necessary. W. D. H.

Bacterial Metabolism. XI. Estimation of Urea Nitrogen in Cultures of Certain Bacteria. ARTHUR I. KENDALL and ARTHUR W. WALKER (*J. Biol. Chem.*, 1913, **15**, 277—282).—Urea nitrogen estimated by Folin's method is probably not all due to urea. In bacteria the main nitrogenous end-product of metabolism is ammonia. The urea nitrogen in the culture fluid does not alter. W. D. H.

Bacterial Metabolism. XIII—XXX. ARTHUR I. KENDALL, ALEXANDER A. DAY, and ARTHUR W. WALKER (*J. Amer. Chem. Soc.*, 1913, **35**, 1201—1249).—An investigation of the effect

of utilisable carbohydrate on the metabolism of protein and protein derivatives by bacteria. The media used consisted of a prepared broth containing meat juice and peptone, and a mixture of the same broth with 1% of dextrose. Four flasks of the sugar-free and of the sugar-containing broths were inoculated with the desired organism and incubated at 37°, the progress of the action being followed by examination of the contents of the flasks over a period of nine days. Determinations were made of the free ammonia, the total nitrogen, the acidity resulting on the addition of formaldehyde, and the acidity or alkalinity of the liquid, using alizarin, neutral red, and phenolphthalein as indicators.

Seventeen groups of bacteria were submitted to examination, and the results are tabulated in the original. D. F. T.

Disinfecting Value of Mercuric Oxycyanide and of Mercuric Oxycyanide Containing Mercuric Cyanide. H. KÜHL (*Arch. Pharm.*, 1913, 251, 340—349).—In general, a solution of a poison at extreme dilution promotes the growth of lower vegetable organisms; at a definite, greater concentration of the poison, the multiplication of the organisms is retarded, whilst at still greater concentrations the poison exerts its lethal action. The author has examined the action on *Bacillus coli* of two samples of mercuric oxycyanide, one practically pure (99%), the other containing 33·3% of oxycyanide and 66·6% of mercuric cyanide. At concentrations of 1 in 200,000 to 1 in 400,000 it is found that solutions of both samples approximately double the rate of growth of the bacilli.

The retarding action of the two disinfectants on the growth of organisms is shown in two ways. Milk coagulates when it contains 0·0005% of either of the two samples, but does not do so when the amount of the poison is increased to 0·005%. In the second set of experiments, urine containing 0·01—0·2% of either of the poisons remains unchanged under the conditions in which the urine alone becomes turbid and evolves ammonia.

Experiments on pure cultures of *Staphylococcus pyogenes*, on raw milk, on tuberculous milk, and on the contents of the stomach and of the intestines and on the brains of a decomposed corpse lead to the astonishing result that there is no appreciable difference in the bactericidal value of the two samples under examination. Another series of comparative experiments shows that the disinfecting value of mercuric oxycyanide is almost equalled by that of a mixture of the oxycyanide and sodium chloride containing 33·3% of the latter. A fuller treatment of the subject is promised; at present the author is of opinion that the sodium chloride, as a disinfectant, slightly active accentuates the bactericidal value of the mercuric oxycyanide by promoting the absorption of the latter substance by the protoplasm. C. S.

Biochemical Reactions of Diphtheria-like Organisms. T. G. M. HINE (*J. Path. Bact.*, 1913, 18, 75—80).—The chief point urged is that the diphtheria-like bacilli, *B. diphtheriae*, alone gives acid with dextrose and dextrin, and not with sucrose.

W. D. H

The Inhibition of the Cholera-Red Reaction by Certain Nitrite-destroying Organisms, and on the Mutual Inhibition of *B. dysenteriae* (Flexner) and *V. cholerae* when Grown together. W. J. LOGIE (*J. Hygiene*, 1913, 13, 162—167).—Certain nitrite-destroying organisms when grown along with *V. cholerae* prevent the appearance of the cholera-red reaction. This is not due to the non-formation of nitrite, but to its rapid destruction by the nitrite-destroying organisms. There are, on the other hand, certain nitrite-destroying organisms which fail to prevent the cholera-red reaction. In the case of *B. dysenteriae* the failure to prevent the cholera-red reaction is due to an inhibition of the growth of both organisms when grown together. W. D. H.

Spore-producing *Bacillus lactis fermentans*, a Ferment Producing Butylene Glycol from Lactose. RUOR (*Compt. rend.*, 1913, 157, 297—299).—*Bacillus lactis fermentans* is a very mobile, anaerobic bacillus, which produces spores after three days on gelose at 30°, which resist a temperature of 90° for five minutes, and can be heated at 100° for half a minute without being killed. It ferments dextrose, sucrose, lactose, mannitol, and glycerol, the products from the sugars being carbon dioxide, hydrogen, alcohol, butylene β -glycol, acetylmethylcarbinol, and formic and acetic acids, no lactic or succinic acids being found. The fermentation of milk by this bacillus is very rapid, the products being as above. W. G.

Isolation of *B. typhosus* from Faeces by means of Brilliant Green. C. H. BROWNING, W. GILMAN, and T. J. MACKIE (*J. Path. Bact.*, 1913, 18, 146—148).—The method described is based on the observation that brilliant-green exerts a much more marked inhibitory effect on *B. coli* than on *B. typhosus*. W. D. H.

Bactericidal Action and Chemical Constitution with Special Reference to Basic Benzene Derivatives. C. H. BROWNING and W. GILMAN (*J. Path. Bact.*, 1913, 18, 144—146).—*Staphylococcus aureus* and *B. anthracis* are more susceptible to basic benzene derivatives than are organisms of the *Coli* group. It is not possible to differentiate generally that gram-positive organisms are susceptible, and gram-negative organisms are not susceptible to crystal-violet. Salts of the heavy metals do not act less powerfully on the colityphoid group than on *S. aureus* and *B. anthracis*. Preliminary details are given of the effects of substituting radicles in benzene derivatives on their bactericidal power; and on the effect of serum on bactericidal action. W. D. H.

Influence of Ozone on Yeast and Bacteria. CARL A. NOWAK (*J. Ind. Eng. Chem.*, 1913, 5, 668).—Results of experiments with bottom-fermentation yeast showed that ozonisation is not only of value in freeing the yeast from objectionable organisms which are susceptible to the action of ozone to a larger degree than the yeast itself, but also in eliminating the weakened cells and stimulating the fermentative power of the surviving ones. W. P. S.

Influence of Mineral Salts on Alcoholic Fermentation. Salts of Tin and Bismuth. MARIUS EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1913, 31, 49—53).—Stannous chloride even in small amounts retards fermentation. Yeast can be acclimatised so as to ferment well in presence of considerably more stannous chloride than will retard fermentation with ordinary yeast; the yeast, however, rapidly degenerates. Stannic chloride is much more toxic than stannous chloride.

With regard to bismuth, the basic nitrate, with which Gimel obtained favourable results, is quite insoluble when washed with hot water.

N. H. J. M.

The Enrichment of the Invertase Content of Living Yeasts. JAKOB MEISENHIMEER, STEFAN GAMBARJAN, and L. SEMPER (*Biochem. Zeitsch.*, 1913, 54, 122—154).—The effect of allowing various yeasts to remain in contact with various sugars on their content in invertase was investigated. It was found that the amount largely increased by this treatment. Large quantities of the organism were allowed to remain for one to two days in sucrose solutions, which were then cooled on ice, and poured off. A portion of the yeast was then removed, the juice expressed and treated with acetone. The invertase reaction constant of this preparation was then determined. The main portion of the yeast was again treated in a similar way, and the reaction constant of a portion also determined; the main bulk was again treated with sugar, and these processes repeated until the yeast was exhausted. During these successive treatments the invertase content increased, although the zymase content diminished. The relative influence of various sugars on the increase of invertase content was also investigated. In the majority of cases, the yeasts were allowed to grow in a Lindner solution, to which was added the various sugars. It was found that in most of the experiments invert sugar and levulose caused a larger increase in the invertase than dextrose or sucrose. The levulose was generally more effective than the invert sugar, and the sucrose slightly more effective than dextrose. The results may possibly be explained on the assumption that a levulose-invertase combination is somewhat more stable than the combination of invertase with other sugars, and the ferment is thereby more efficiently guarded against change during the autolysis of the yeast.

S. B. S.

The Dominance of Roquefort Mould in Cheese. CHARLES THOM and JAMES N. CURRIE (*J. Biol. Chem.*, 1913, 15, 249—258).—The low percentage of oxygen in the open spaces within the cheese accounts for the dominant activity of *Penicillium roqueforti* in Roquefort and similar cheese. Gas analyses from cultures of various kinds of moulds are presented.

W. D. H.

Phenomena of Imbibition in the Seeds of *Avena sativa*. F. PLATE (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 133—140).—From experiments with solutions of potassium, sodium, barium,

and calcium hydroxides, and of hydrochloric, nitric, sulphuric, and phosphoric acids, the author finds that both cation and anion have specific functions in regard to this phenomenon. The solutions accelerate germination, and considerable concentrations do not spoil germination, but even favour it.

R. V. S.

Compounds Obtained from Plant Seeds by the Methods for Extracting Lecithin. IV. Peas, Larch, Rice. GEORG TÄGER (*Zeitsch. physiol. Chem.*, 1913, **86**, 407—414).—Peas contain rather over 1% of lecithin. This yielded galactose on acid hydrolysis and colamine when hydrolysed with barium hydroxide.

The lecithin from larch seeds contained about 3.3% of phosphorus, 0.75% of nitrogen, and 4% of galactose.

Rice which had not been deprived of the husk yielded a lecithin compound having the properties of a cerebroside.

E. F. A.

Distribution of Carboxylase in Plants. W. ZALESKI (*Ber. deut. bot. Ges.*, 1913, **31**, 349—353).—Carboxylase was found in various seeds, such as peas, lupines, *Vicia Faba*, wheat, and maize, in etiolated seedlings, and in moulds.

Although anærobic, carboxylase is active in presence of oxygen; and some of these substances decompose pyruvic acid equally well in air and in hydrogen. Some, however, such as ripening pea seeds, fail to decompose pyruvic acid in presence of air, whilst they are very active in a vacuum. The stem points of *Vicia Faba* decompose pyruvic acid in presence of air if previously extracted with methyl alcohol.

N. H. J. M.

Chemical Composition of Cooked Vegetable Foods. KATHARINE I. WILLIAMS (*J. Ind. Eng. Chem.*, 1913, **5**, 653—656).—Analyses of cooked vegetables, cereals, and leguminous seeds, etc., are recorded (compare P., 1903, **19**, 26).

W. P. S.

Chlorophyll Assimilation. K. von KÖRÖSY (*Zeitsch. physiol. Chem.*, 1913, **86**, 368—383).—In acacia leaves immersed in nutritive fluids the assimilation of starch and sugar was about 10%, but the fat in the leaves was not increased.

W. D. H.

Composition of the Fruit and Seeds of *Adansonia digitata*. RUSSELL GEORGE PELLY (*J. Soc. Chem. Ind.*, 1913, **32**, 778—779).—The seeds of the baobab tree (*Adansonia digitata*) consist of a very tough husk enclosing a soft, oily kernel, devoid of starch. Analysis gave, in percentages: moisture, 12.1; ash, 3.5; oil, 11.6; protein (total nitrogen multiplied by 6.25), 11.2; fibre, 22.5; carbohydrates (by difference), 39.1. The ash of the kernels contained: potash, 31.0; soda, 7.2; and phosphoric acid, 34.2%. The oil as extracted by light petroleum had D_4^{20} 0.915, saponification value, 190.5—191.7, and iodine value (Hübl, seventeen hours), 76.7—77.8. The seeds are free from alkaloids and cyanogenetic glucosides.

The fruit pulp gave: moisture, 15—16%; ash, 4.76—6.10%;

matter soluble in alcohol, 16.7–18.7%. The ash consisted largely of alkali carbonates, and contained: silica, 4.74; lime, 8.88; potash, 48.90; soda, 4.20; and phosphoric acid, 1.08%. The pulp consisted largely of pectous matter. The free acid extracted by 95% alcohol was found to be citric acid; no indications of tartaric acid were obtained, but small amounts of malic acid may be present. The pulp also contains an acid or acids of the pectic type, possibly present as acid potassium salts and insoluble in alcohol. T. S. P.

Application of the Biochemical Method to the Detection of Sucrose and Glucosides in Certain Ericaceæ. ÉMILE BOURQUELOT and (Mlle.) A. FICHTENHOLZ (*J. Pharm. Chim.*, 1913, [vii], 8, 158–164).—The presence of sucrose, of a β -glucoside which is hydrolysed by emulsin, and of invertase and emulsin is demonstrated in *Arbutus unedo*, *Arbutus Menziesii*, *Azalea mollis*, *Calluna vulgaris*, *Kalmia latifolia*, and *Vaccinium myrtillus*. E. F. A.

Plant Chemistry. P. Q. KEEGAN (*Chem. News*, 1913, 108, 61–62. Compare A., 1912, ii, 1085).—A brief résumé and discussion of our present knowledge of the occurrence and composition of the bitter principles, fat-oils, and oxydases in plants, special reference being made to analyses of the bearberry (*Arbutus uva-ursi*). W. G.

The Nature of the Sugar Found in the Tuber of Arrowhead. K. MITAKE (*J. Biol. Chem.*, 1913, 15, 221–229).—Dextrose, levulose, and sucrose were found; galactose and raffinose are doubtful; maltose, pentose, and mannose are absent. W. D. H.

Capoc Seeds and Capoc Oil. HERMANN MATTHES and HEINRICH HOLTZ (*Arch. Pharm.*, 1913, 251, 376–396).—Capoc seeds, obtained from *Eriodendron anfractuosum* and other trees and plants allied to the *gossypium*, contain 7.5% of water, 25.6% of fatty oil, and 5.6% of ash; the last consists essentially of potassium phosphate, and contains also considerable quantities of calcium, magnesium, and sulphuric acid. Capoc oil, which is expressed from the seeds, is a pale yellow, viscous liquid, having a faint, pleasant odour and taste; after long keeping it deposits solid constituents. It resembles cotton-seed oil, with which it is often adulterated. The oil has D_{20}^{25} 0.9218, n_D^{40} 1.4630, and is optically inactive. It has iodine number 88.7 (93.3) [the numbers in brackets are the values given by a capoc oil extracted from the seeds by petroleum], acid number 21.6 (3.4–4.6), saponification number 192.3 (196.3), Reichert-Meißl value 0.8, and Polenske value 0.14–0.34. The m. p. of the fatty acids (Hehner's method) is 34–35° and the solidifying point 28–30°, the values of the m. p. and of the solidifying point being 36° and 31–32° respectively after the acids have been freed from phytosterol. The very high m. p. of the fatty acids serves to identify capoc oil in the presence of other oils, as also do Halphen's reaction Milliau's modification of Becchi's reaction, and the nitric

acid test. The behaviour of the oil with Welman's, Serger's, and Kreis's reagents, and in the elaidic acid test is also described. Capoc oil is a drying oil, but does not become hard even after four months' exposure.

Capoc oil consists essentially of the triglycerides of palmitic, oleic, and linolic acids. The fatty acids are 26—28% palmitic acid and 72—74% liquid acids (40% linolic acid and 60% oleic acid); volatile acids are present only in small quantity. The oil contains 1.04% of unsaponifiable matter.

The crude phytosterol obtained from the oil contains 74% of reddish-brown, slightly dextrorotatory liquid constituents (iodine number 74.7), and 26% of a solid *phytosterol*, m. p. 136°, $[\alpha]_D -29.97^\circ$ in alcohol and ether (*acetate*, m. p. 126°, needles).

C. S.

Presence of Quinine in the Seed of Cinchona Ledgeriana (Moens). P. VAN LEERSUM (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 153—155).—In order to investigate the formation of quinine in *Cinchona* the author has examined the seeds of *C. Ledgeriana*. The finely powdered seed was first extracted with light petroleum, which removed a pale green oil, $D^{15} 0.930$, $[\alpha]_D -26^\circ$, which formed 18.6% of the material, and then digested with lime and sodium hydroxide and extracted with benzene. The total alkaloid so obtained (about 0.38% of the dry seed) was purified, and finally concentrated as the hydrochloride on a microscope slide, when quinine was detected by the herapathite reaction (compare A., 1905, ii, 620).

J. C. W.

The Availability of Glucosamine Hydrochloride as a Source of Nitrogen for the Nutrition of Maize (*Zea Mays*) and Beans (*Phaseolus multiflorus*). MARSTON LOVELL HAMLIN (*J. Amer. Chem. Soc.*, 1913, 35, 1046—1049).—When, for the purpose of comparison, the above-named plants were grown in an ordinary culture solution, in a nitrogen-free solution and in a solution containing glucosamine hydrochloride as the sole source of nitrogen, it was invariably found that the glucosamine had a deleterious effect, and caused withering.

It is evident, therefore, that under the conditions of the experiment, glucosamine cannot be utilised as a source of nitrogen for nutrition.

D. F. T.

A New Species of Prostanthera and its Essential Oil. R. T. BAKER and HENRY G. SMITH (*J. Roy. Soc. New South Wales*, 1913, 46, 103—110).—The stalks and leaves of the new shrub, for which the name *Prostanthera cincolifera* is proposed, yield 0.71% of a yellow oil, which rapidly darkens on exposure to light. The crude oil has $D^{15} 0.9204$, $n_D^{22} 1.4711$, and is soluble in 1.7 volumes of 70% alcohol. After removal of phenols and aldehydes, the cleared oil has $D^{15} 0.9199$; $n_D^{22} 1.4706$, $\alpha_D +4.1^\circ$. Saponification number of ester + free acid = 9.9 by boiling and 8.5 by cold saponification with two hours' contact; saponification number after acetylation 34.2 by

boiling, 18.3 by cold saponification. It is probable that the principal ester in the oil of this plant is geranyl acetate, constituting 2.9% of the crude oil. The isolation of geraniol was not, however, practicable owing to the small quantity of oil obtainable. The phenols present constitute 0.65% of the oil, and are composed of carvacrol and thymol. Cuminaldehyde is present to the extent of 0.142%.

The main constituents of the oil are cineole (61 per cent.) and cymene. A small quantity of a dextrorotatory terpene, probably pinene, is also present, whilst, by the action of alcoholic potassium hydroxide on the portion of the oil boiling above 224°, a substance is obtained which is possibly a sesquiterpene, but the amount of which is insufficient for identification.

H. W.

Condition of Soil Phosphoric Acid Insoluble in Hydrochloric Acid. WILLIAM H. FRY (*J. Ind. Eng. Chem.*, 1913, 5, 664—665).—Whilst it is probable that soils may contain small quantities of phosphoric acid compounds which are not soluble in hydrochloric acid, mineralogical analyses have shown that a very large number of soils contain apatite (a soluble phosphate) enclosed in quartz grains. The quartz acts as a protective coating, and the phosphate is apparently insoluble in hydrochloric acid.

W. P. S.

Organic Soil Constituents in their Relation to Soil Fertility. OSWALD SCHREINER (*Eighth Inter. Cong. App. Chem.*, 1912, 15, 231—245).—In water-culture experiments with wheat, it was shown that creatinine, creatine, hypoxanthine, arginine, histidine, and nucleic acid are all assimilated, both when supplied as the only source of nitrogen and in presence of nitrate. When nitrates are present in addition to the organic compounds, there is a decrease in the amount of nitrate assimilated as compared with the amount when nitrate alone is supplied. The lowest decrease in nitrate absorbed was 17% with creatine, and the highest, 45%, with hypoxanthine. Further experiments on the effect of histidine, creatinine, and asparagine, used singly and together, showed increased growth with the single substances, in the order as given; and a further increase when all were present simultaneously, although the amount of nitrogen supplied was the same.

N. H. J. M.

Organic Phosphorus in the Soil. JOHN STEWART (*Eighth Inter. Cong. App. Chem.*, 1912, 15, 273—300).—The Grandeau method for estimating organic phosphorus in soils gives somewhat low results, since some of the phosphorus dissolves in the acid, and some remains undissolved after treatment with alkali. The method is, however, one of the best hitherto proposed.

The iron and aluminium of humus are organically combined, except the small amount in colloidal form.

The decaying organic matter of soils interacts with the phosphates present with production of various organic compounds containing phosphoric acid and the different bases. Acid and basic mineral phosphates are probably found as intermediate products.

Barium chloride, magnesia mixture (both in alkaline solutions), phenylhydrazine in faintly acid solution, and ammonium hydroxide in presence of sufficient iron or aluminium, reprecipitate inorganic phosphorus quantitatively in presence of organic matter, in some cases at least. No precipitate is formed in absence of organic matter.

N. H. J. M.

Biochemical Factors in Soils. MICHAEL X. SULLIVAN (*Eighth Inter. Cong. Appl. Chem.*, 1912, 15, 305—312).—The oxidising power of soils, as indicated by aloin, is greater in productive than in less productive soils, and in surface soils as compared with subsoils. The catalytic power of soils shows similar differences.

It is evident from the presence of such compounds as histidine, arginine, and cytosine, that soils contain enzymes, either intra- or extra-cellular. No soil extract has hitherto been found to contain diastatic, inverting, lipolytic, proteolytic, oxidising, or catalysing enzymes; and it has been found that when diastase is added to soil it is either fixed or destroyed in a few days.

The oxidising and catalysing powers of soils are probably due to the inorganic and organic substances rather than to enzymes. Both properties are retained for years by air-dried soils. Many substances present in soils result from the metabolism of micro-organisms. In mould cultures, fatty acids, especially oleic and palmitic acids, purine bases, such as guanine, adenine, and hypoxanthine, histidine, and probably thymine, are present.

N. H. J. M.

Increasing the Manurial Action of Cyanamide under the Influence of Ferric Oxide. ALBERT STUTZER (*Eighth Inter. Cong. App. Chem.*, 1912, 15, 301—304).—The results of pot experiments with oats grown in sandy loam showed that the manurial value of cyanamide is increased by addition of molasses, owing to the increased production of carbon dioxide in the soil.

In further experiments, it was found that addition of ferric oxide, in the form of bog ore, greatly increased the yield of oats. It was found that ferric oxide accelerates the production of carbamide from cyanamide, and there may be a stimulating action in addition.

As a rule, 50 kilos. of bog ore per hectare will suffice.

N. H. J. M.

Boron as Catalytic Manure. HENRI AGULHON (*Eighth Inter. Cong. App. Chem.*, 1912, 15, 9).—In pot experiments with peas, haricots, beet, and radish, the yields were increased by boric acid up to 34%. In field experiments with oats, the yield was increased by 54% when 1.5 kilo. of boric acid per hectare was applied. Applications of 20—50 kilos. were found to be too much for wheat, oats, maize, lucerne, peas, colza, and lupines; the yields, weighed fresh, were frequently increased without any gain in dry matter.

N. H. J. M.

General and Physical Chemistry.

Constancy of the Refraction Equivalents. KARL VON AUWERS and FRITZ EISENLOHR (*Zeitsch. physikal. Chem.*, 1913, 83, 429—441).—The authors have re-determined the refraction equivalents for the atoms carbon, hydrogen, and oxygen, and for the methylene group, using carefully purified substances. They show that for practical purposes the values are constant, although strictly this is not the case. Constitutive influences make themselves noticeable to a slight extent. Thus, in the case of the *cycloparaffins*, it is shown that the entrance of a methylene group raises the refraction equivalent; this increase is noticeable in every case except when the methyl groups are in the *gem*-position. Thus, for the substances *cyclohexane*, *methylcyclohexane*, 1:4-dimethylcyclohexane, and 1:3:5-trimethylcyclohexane, the values are H_e : 4.597, 4.620, 4.638, 4.644. The 1:2-derivatives give lower values than the 1:3, and these lower than the 1:4, whereas the *gem*-compounds give still lower values. J. F. S.

Further Remarks on a Formula for the Index of Refraction of Binary Mixtures. FRÉDÉRIC SCHWERS (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 513—517. Compare this vol., ii, 453).—Polemical. A further reply to Mazzucchelli (this vol., ii, 165). R. V. S.

Character of the Double Refraction of Pleochroic Liquid Crystals. DANIEL VORLÄNDER and M. E. HUTH (*Zeitsch. physikal. Chem.*, 1913, 83, 424—429. Compare A., 1906, ii, 337; 1908, ii, 88; 1911, ii, 165; also Dorn, A., 1910, ii, 809).—The authors have examined the double refraction of a number of substances forming liquid crystals, and in most cases it is shown that two or more liquid crystal forms exist. The change of one form to another by heating and cooling is indicated diagrammatically. Thus, for the active myl ester of *p*-anisylideneamino- α -methylcinnamic acid, the changes are:

Amorph. liquid \leftarrow Cryst. liquid II \leftarrow Cryst. solid I.

Cryst. liquid I \rightarrow Cryst. liquid II \rightarrow Cryst. solid II.

Crystalline liquids I and II are pleochroic.

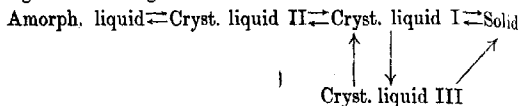
Active amyl ester of *p*-ethoxybenzylideneamino- α -ethylcinnamic acid gives the changes:

Amorph. liquid \leftarrow Cryst. solid.

Cryst. liquid I \rightarrow Cryst. liquid II \rightleftharpoons Cryst. liquid III.

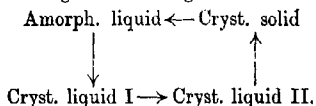
Crystalline liquids I and II are pleochroic.

Active amyl ester of *p*-ethoxybenzylideneamino- α -methylcinnamic acid gives the changes:



Crystalline liquids I and II are pleochroic.

Cholesteryl chloride gives the changes:



Crystalline liquids I and II are pleochroic. From the examination of the double refraction the authors are able to confirm the result of Vorländer (*loc. cit.*) that the double refraction is negative in those cases where two pleochroic liquid crystal phases are found for the same substance.

J. F. S.

Magnetic Birefracton of Liquid Mixtures. A. CORTON and HENRI MOUTON (*Compt. rend.*, 1913, 156, 1456—1459. Compare this vol., ii, 288).—The law of additivity cannot be rigorously applied to the magnetic birefracton of a mixture of liquids. Nitrobenzene, when diluted with inactive liquids, such as carbon tetrachloride or alcohol, gives values far below the calculated, whereas α -bromonaphthalene similarly diluted gives values above those calculated. A mixture of equal volumes of nitrobenzene and α -bromonaphthalene gives values fairly closely in accord with those calculated.

W. G.

The Goldstein Method of Producing Fundamental Spectra and the Spectra of Air, Nitrogen, and Oxygen in Geissler Tubes. JOSEPH SCHARBACH (*Zeitsch. wiss. Photochem.*, 1913, 12, 145—205. Compare Goldstein, A., 1910, ii, 669).—The object of the present paper is to control the work of Goldstein (*loc. cit.*) with regard to the spectra of salts in Geissler tubes. It was necessary before this could be done that the spectra of air, oxygen, and nitrogen should be determined. The author has therefore determined the spectra of air, oxygen, and nitrogen in Geissler tubes, and also the spark spectra of air, using aluminium poles. The measurements were made by means of a concave Rowland grating of 1.80 metre radius of curvature, and the spectra photographed. It is shown that lines appear in spark spectrum of air which are not to be found in the spectrum from the Geissler tube, and vice versa; also many lines are found strengthened in the Geissler tube, whilst the strengthening of tube lines in the spark is rarely found. The second part of the paper deals with the spectra of caesium bromide, potassium chloride, fluoride, iodide and bromide, sodium chloride, bromide, iodide and fluoride, lithium chloride, bromide and iodide, barium chloride, and silver nitrate in Geissler tubes.

between λ 3000 and λ 5900. The measurements were made in the same manner as Goldstein's, but the results differ from his in essential points. The air lines are to be found in all the spectra, and the metal and non-metal lines are not new, but correspond with hitherto measured lines of these elements. The lines termed by Goldstein "Fundamental Spectrum" lines therefore do not exist under the conditions of these experiments. Tables of all the wave-lengths measured are given, and these are compared with the values of other observers.

J. F. S.

The Origin of Bands in the Spectrum of Active Nitrogen. E. PERCIVAL LEWIS (*Phil. Mag.*, 1913, [vi], 25, 826—832. Compare A., 1900, ii, 702; also Strutt and Fowler, A., 1911, ii, 678).—The author shows that with approximately pure nitrogen the spectrum of the third group of nitrogen bands could not be obtained in any circumstances, but when a small percentage of oxygen was admitted they invariably appeared when the discharge was weak, and in addition the β -group of Strutt and Fowler also appeared whenever the third group was present. In studying the after-glow, it was seen that the spectrum contained every band observed by Strutt and Fowler, as well as the "fourth positive group of bands" first observed by the author and Strutt and Fowler. The fourth positive group bands are only found in the spectrum of the discharge which produces the after-glow, and not in the spectrum of the after-glow itself. A series of photographs of the spectra are given, and from these it appears that the second group of bands belong entirely to the discharge and not to the after-glow, whilst the third group and the β -groups are relatively more intense in the after-glow. The author doubts whether pure nitrogen has ever been used in the work on nitrogen spectra.

J. F. S.

An Undescribed Spectrum? Probably? Belonging to Helium. JOSEPH GOLDSTEIN (*Ber. Deut. physikal. Ges.*, 1913, 15, 402—412).—The author describes a spectrum which he has observed with helium drawn from many sources. The spectrum is best seen and photographed in an "end on" tube which has a wide cross section. Details and photographs are given of the spectrum obtained in a 2 mm. wide tube at pressures of 30—50 mm., using a condenser spark gap in the circuit. The spectrum appears to have the same relationship to the series spectrum that the second hydrogen spectrum has to the hydrogen series spectrum.

J. F. S.

Electric Behaviour of Certain Vapours with Banded Absorption. JOHANNES STARK (*Physikal. Zeitsch.*, 1913, 14, 44—456).—Polemical against Burger and Koenigsberger (this vol., 85).

H. M. D.

Distribution of the Light Emission in an Arc Between Metal Poles for Wave-lengths Below λ = 4000. HEINRICH BREMANN (*Zeitsch. wiss. Photochem.*, 1913, 12, 65—76, and 13—143).—The arc spectra of a number of metals were photo-

graphed by means of a quartz spectrograph, and the intensity of the lines compared at the poles and the centre. A full description of the instrument and method is given. The following metals were examined: tin, zinc, lead, calcium, thallium, cadmium, magnesium, aluminium, copper, and silver. The presence of many spark lines are found in all the spectra, and this fact, which had previously only been observed in a few cases, may be taken as general for arc spectra. It is shown that in a given spectrum, taking the lines along their length from pole to pole, that some are of uniform intensity; others have an intensity which is greater at one or other or both poles; the strengthening at the poles may or may not be the same. It is also shown that all types may occur in a given spectrum. The relative intensity of the various elements in different parts of the lines can be seen from the comparative scheme:

(a) Sn 0, Ag 2.3, Cu 3.5, Tl 4.4, Pb 9.5, Cd 21.9, Ca 28.6, Mg 34.2, Zn 40.7, and Al 100.0 indicates the percentage of lines which are strengthened at the positive pole.

(b) Al 0.0, Cd 7.1, Zn 7.4, Mg 7.9, Pb 15.6, Ca 39.0, Cu 51.7, Sn 70.4, Ag 84.7, and Tl 87.0 indicates the percentage of lines which are strengthened at the negative pole.

(c) Al 0.0, Ag 12.9, Tl 17.4, Sn 31.5, Ca 32.4, Cu 44.7, Zn 51.8, Mg 57.9, Cd 74.0, and Pb 78.2 indicates the percentage of lines which are of equal intensity at both poles.

The lines which are not strengthened are mainly arc lines. The lines which show the greatest differences, or only appear at the poles, are all enhanced lines of the spark spectra. The majority of the lines which are strengthened at the poles are to be found in the extreme ultra-violet. The intensity ratio of the spark lines in the arc spectrum is different from the ratio of the enhanced lines in the spark spectrum. The author shows that the enhanced lines are to be divided into several groups, and he is of the opinion that the appearance of spark lines near the poles explains the differences in arc spectra of other observers. The spectral relationships are compared with the melting points, boiling points, specific gravities, atomic weights, electro-potential and chemical properties of the elements examined, but no definite relationship is to be found. In the case of the electro-potential, there is a partial similarity in the order of the elements. The various reasons for the differences in the intensity are discussed, and lead the author to the conclusion that neither the potential fall distribution, temperature distribution, nor any other single cause can explain the appearance of the spark lines.

J. F. S.

Measurement of the Spark and Arc Spectrum of Calcium on the International Normal. OSWALD HOLTZ (*Zeitsch. wiss. Photochem.*, 1913, 12, 101—123).—The spectrum of calcium was determined, using a concave Rowland grating of 6.4 metre radius of curvature and 20,000 lines per inch. The spectrum was photographed, and the wave-lengths determined by a measuring machine. For the arc spectrum, hollow carbon poles filled with calcium carbonate, or solid carbon poles with calcium chloride laid on the

lower carbon, were used, and for the spark spectrum calcium poles were employed. The arc was fed with a current of 7 amperes at 220 volts, and the spark obtained from a resonance transformer fed by alternating current. In the earlier work it was found that a given line did not give the same value for the wave-length when measured on different occasions. Investigation into the cause of this showed that temperature changes in the grating room were responsible, hence in the work precautions were taken to keep the temperature constant. A full list of the lines is given, and compared with the values of Kayser, Rowland, Exner and Haschek, Eder and Valenta, and Saunders. A complete bibliography is appended to the paper. J. F. S.

Arc Spectrum of Iron. KEVIN BURNS (*Zeitsch. wiss. Photochem.*, 1913, 12, 207—235).—The object of this paper is to measure all lines of the iron spectrum which can be easily photographed. The stronger lines were photographed and measured four times; the lines above 5434 are not included in the paper owing to the absence of a sufficiently accurate normal. The measurements are made with a Rowland grating of 635 cm. focus and 787 lines per cm. Many pairs are found the distance of which apart is not greater than λ/n . 110,000 of the theoretical dispersing power, and in numerous pairs with twice this distance the single lines are separated clearly by a bright space. The lines are given in tables together with some manganese and nickel lines. J. F. S.

Spectrum Absorption and Polymorphism. KARL SCHAUM (*Zeitsch. wiss. Photochem.*, 1913, 12, 143—144).—The author indicates the possibility of deciding between chemical polymorphism and physical polymorphism by means of absorption or luminescence spectra, and he sees in this method a means of deciding between the views of Tammann (this vol., p. 193) and Smits (A., 1910, ii, 195, 400; this vol., p. 393) with regard to polymorphism. J. F. S.

Absorption Spectra of Manganese Salts in Different States of Oxidation. WALTER JÄESCHKE and JULIUS MEYER (*Zeitsch. physikal. Chem.*, 1913, 83, 281—289).—An attempt is made to find a relationship between the colour of derivatives of manganese compounds and the valency it is exhibiting in these compounds. For this purpose the absorption spectra of potassium permanganate, potassium manganate, the doubtful manganese tetrachloride, manganic chloride, manganic sulphate, manganic phosphate, manganous chloride, and manganous sulphate are determined. The absorption spectra of all the compounds show great similarity, particularly in respect of the band in the red; this band is very persistent, and only disappears with the very dilute solutions of permanganate and manganous chloride. The central band appears, however, to be influenced by the valency, in the sense that it moves toward the red end of the spectrum with increasing valency. The authors state that the violet end of the spectrum is most sensitive to changes in valency, but they were unable to make any

measurements in that region or in the ultra-violet portion of the spectrum. J. F. S.

Absorption Spectra of Six Blue, Green, and Violet Dyes Sanctioned for Use in Confectionery. GUSTAVE MASSOL and A. FAUCON (*Bull. Soc. chim.*, 1913. [iv], 13, 513—519).—The method of investigation used is that already described (this vol., ii, 264). Malachite-green, acid-green-J and patent-blue show three bands, one in the visible spectrum, one at the point between the visible and invisible portions of the spectrum, and one in the ultra-violet. Water-blue-6B is characterised by a large band ($\lambda = 320$ to 275) in the ultra-violet, similar to that shown by acid-magenta. Paris-violet and acid-violet-6B have a single absorption band in the visible portion of the spectrum. The limits of the bands for each dye are shown by tables and graphs. T. A. H.

Absorption of the Ultra-violet Rays by the Alkaloids of the Atropine Group. MARCEL GOMPEL and VICTOR HENRI (*Compt. rend.*, 1913, 156, 1541—1544).—A quantitative study of the absorption of the ultra-violet rays by the three alkaloids atropine, apoatropine, and cocaine. The measurements were made with alcoholic solutions, and the molecular constants of absorption calculated for the maxima and minima of absorption. The spectrum of atropine presents three absorption bands at $\lambda = 2645$, 2580, and 2505 respectively. Above $\lambda = 2493$ the absorption steadily increases. These three bands correspond with three in the benzene spectrum moved slightly towards the red. This alkaloid can be detected at a dilution of 5 parts in 10,000. apoAtropine has a much stronger absorption than atropine. Its spectrum exhibits one band at $\lambda = 2626$, and by means of it the alkaloid can be detected at a dilution of 2 parts in 10,000. The spectrum of cocaine is sharply distinguished from the two previous ones. It possesses three absorption bands at $\lambda = 2814$, 2722, and 2314 respectively, the one at $\lambda = 2314$ being extremely intense, having a molecular constant of absorption greater than 20,000. These three bands correspond with three in the spectrum of benzoic acid moved slightly towards the red. The band at $\lambda = 2314$ permits of the detection of 1 part of cocaine in 200,000 of solution. W. G.

The Relationship Between the Absorption, Dispersion, and Fluorescence of Light. BENKT SÖDERBERG (*Ann. Physik.*, 1913. [iv], 41, 381—402).—A description is given of measurements of the extinction-coefficient, absorption spectra, and refractive index of solutions of eosin (sodium salt), fluorescein, and erythrosin in water and acetone-water solutions. The experiments were carried out at ordinary temperatures, and in case of the absorption spectra of eosin in water solution, also at 40°, 60°, and 80°. It is shown that the absorption bands of the non-fluorescent solutions can be resolved into two elementary bands, which the author numbers 1 and 3; No. 1 lying toward the violet, and No. 3 toward the red end of the spectrum. The absorption bands of the fluorescent

solutions exhibit two maxima; the one maximum *B* dominates the spectrum, and can be resolved into three elementary bands, No. 2 lying between 1 and 3, and this new band together with 3 together constitute the maximum *B*. Solutions, which on dilution pass from the non-fluorescent to the fluorescent condition, do not obey Beer's Law. At greater concentrations, when the absorption gives no indication of the passage to fluorescence, and also when the fluorescence is strongly marked, the solutions obey Beer's law. The absorption bands of erythrosin and fluorescein solutions show a somewhat higher maximum for *B* than for *A*. This indicates that they are in the condition when they are about to pass into the fluorescent condition, although there is no indication of elementary band 2. On the other hand, this band makes itself very noticeable in the dispersion curve. The presence of band 2 in the absorption spectrum is made probable on the assumption that the absorption is neutralised by the fluorescence. The absorption bands of a 10% eosin water solution shows two equal maxima, and its observed dispersion curve agrees well with the calculated curve. From this it is concluded that there is no band 2 or at most only a very weak one, and that here there is no latent fluorescence. The following general conclusions are deduced: (1) Fluorescence is occasioned by absorption in the elementary band 2. (2) Fluorescence can be strong but latent in concentrated solutions. (3) On dilution the latent fluorescence shifts toward the red, the elementary band 2 appears, and the fluorescence becomes visible. These results are in accordance with Stark's theory of the coincidence of the absorption and fluorescence spectra for short wave-length bands. Both the dispersion formulæ of Ketteler and Helmholtz are in accordance with the view of latent fluorescence.

J. F. S.

Rotational Optical Activity of Solutions. G. H. LIVEN (Phil. Mag., 1913, [vi], 25, 817—826).—A theoretical paper in which the author, from the electromagnetic theory, deduces an equation which expresses the rotatory power of a dissolved substance. The three equations of Landolt are shown to be approximations of the formula evolved, and to represent special cases. A few discrepancies between experimental facts and those deduced from the formula are indicated. These occur particularly at the minimum value of the rotation.

J. F. S.

Studies of the Processes Operative in Solutions. XXVII. The Causes of Variation in the Optical Rotatory Power of Organic Compounds and of Anomalous Rotatory Dispersive Power. HENRY E. ARMSTRONG and E. E. WALKER (Proc. Roy. Soc., 1913, A, 88, 388—403).—The authors summarise their views as follows: The variations in rotatory power met with in optically active compounds may be ascribed (a) to alterations in molecular size, and to the formation of compounds between solvent and solute; (b) to the occurrence of changes giving rise to the presence of reversibly related isodynamic forms.

The changes included under (a) are common to all optically

active substances; those included under (b) can occur only in special cases. In these special cases, if the change involve the formation of compounds so different in chemical type that they not only differ in rotatory power in sign but also in rotatory dispersive power, the product might have anomalous dispersive power; in other cases it would behave normally.

The above conclusions are drawn from a consideration of the specific rotations in solution of lævulose, methyl and ethyl tartrates, o-nitrobenzoyltetrahydroquinoline, and 2-nitrotoluene-4-sulphonyl-tetrahydroquinoline.

T. S. P.

Magneto-chemical Researches. III. PAUL PASCAL (*Ann. Chim. phys.*, 1913, [viii], 28, 218—243).—A continuation of the résumé already abstracted (A., 1912, ii, 426). This portion gives in greater detail a discussion of the results obtained with acetylenic compounds, and corrects certain of the values already given (A., 1912, ii, 734). An examination of a number of allyl compounds shows that the mean value of λ for the double linking in the allyl group is $+47 \times 10^{-7}$, as compared with $+57 \times 10^{-7}$ for the ordinary ethylenic linking. The figures for allyl alcohol and for diacrolein-acetylene, $\text{CH}_2\text{:CH}\cdot\text{CH}(\text{OH})\cdot\text{C}\equiv\text{C}\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{CH}_2$, are anomalous.

T. A. H.

Variations of the Magnetic Rotatory Power with Changes of State. J. CHAUDIER (*Compt. rend.*, 1913, 156, 1529—1532. Compare this vol., ii, 368).—A comparative study of the magnetic rotatory power of substances in the gaseous and liquid states and in the liquid and solid states. The magnetic rotatory power in the gaseous state, as calculated from the values in the liquid state, supposing that the phenomenon varies as the density, is found to be higher than the observed value in the case of oxygen, carbon dioxide, and carbon disulphide, substances for which the magnetic rotatory dispersion is in wide disagreement with the law of the inverse square of the wave-length, whilst in the case of nitrogen, sulphur dioxide, and chloroform, which obey this law, the observed and calculated values agree fairly closely. In the passage from the liquid to the solid state the magnetic rotatory power disappears completely in the case of active liquids, which solidify to crystalline solids, but is preserved unaltered where the liquids give amorphous, vitreous solids.

W. G.

Determination of the Order of a Photochemical Reaction. A. TIAN (*Compt. rend.*, 1913, 156, 1758—1761).—A theoretical paper, in which the author shows that it is possible to deduce mathematically the order of a photochemical reaction.

W. G.

The Decomposition of Lactic and Tartaric Acids in Ultra-violet Light. HANS EULER and S. RYD (*Biochem. Zeitsch.*, 1913, 51, 97—106).—Lactic acid, in the presence of the short ultra-violet rays, undergoes a decomposition, analogous to a fermentation, with evolution of carbon dioxide. This reaction is less influenced by

temperature than other photochemical reactions. The rate of evolution of carbon dioxide is not accelerated by the presence of either ferrous or ferric salts, but the latter are reduced. Tartaric acid undergoes similar changes in the ultra-violet light, with the formation of carbon dioxide and reducing substances. In this case ferric (but not ferrous) salts increase the rate of gas evolution, being reduced themselves at the same time.

S. B. S.

Chemical Action of Light. XXVI. Autoxidations. IV. GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1913, 46, 1558—1565; *Atti R. Accad. Lincei*, 1913, [v], 22, 539—547. Compare A., 1912, i, 174, 645; this vol., i, 350).—The authors have studied the spontaneous oxidation of aqueous solutions of hydroxy-acids in light in the absence of other substances, such as salts of iron or uranium (contrast Neuberg, A., 1908, ii, 915; Benrath, A., 1911, ii, 681).

Lactic acid, in these circumstances, yields carbon dioxide and acetaldehyde, identified as the *p*-nitrophenylhydrazone, m. p. 127—128°. Acetic acid is also formed.

Mandelic acid gives carbon dioxide, benzaldehyde (characterised by its semicarbazone, m. p. 216°), salicylaldehyde, benzoic acid, and salicylic acid.

Carbon dioxide, formaldehyde (*p*-nitrophenylhydrazone, m. p. 180°), acetaldehyde, formic and acetic acids are formed by the oxidation of malic acid.

The volatile products of the oxidation of tartaric acid consist of carbon dioxide and formic acid. From the non-volatile products, the osazone of hydroxypyruvic acid, m. p. 208—209° (*sodium salt*, orange-yellow needles, m. p. 239°), and glyoxalosazone, m. p. 175°, were obtained by means of phenylhydrazine acetate.

Citric acid yields carbon dioxide and acetone (*p*-bromophenylhydrazone, m. p. 92°).

Quinic acid (tetrahydroxycyclohexanecarboxylic acid) gives quinol and 3:4-dihydroxybenzoic acid in accordance with the equations: (1) $C_6H_7(OH)_4CO_2H + O = C_6H_3(OH)_3 + CO_2 + 3H_2O$, and (2) $C_6H_7(OH)_4CO_2H + O = C_6H_3(OH)_3CO_2H + 3H_2O$.

Carbon dioxide, formic acid, and the semialdehyde of maleic acid are formed from pyromucic acid. The latter product was identified in the form of its phenylhydrazone, m. p. 157° (which was identical with the product obtained by the action of phenylhydrazine on the semialdehyde of maleic acid obtained by treatment of pyromucic acid with bromine in alkaline solution), and also as the oxime, m. p. 130°, which was subsequently converted into methyl fumarate, m. p. 102°.

Cinnamic acid yields α -truxillic acid, benzaldehyde, benzoic, and formic acids.

The authors are unable to confirm Inghilleri's statement (A., 1911, i, 354) that a sugar-like substance (sorbosc) is formed when formaldehyde (40%) and crystallised oxalic acid are exposed to sunlight.

H. W.

Chemiluminescent Reactions with Physiological Substances. F. ALEX. McDERMOTT (*J. Amer. Chem. Soc.*, 1913, 35, 824—826)

—When solid potassium cyanide is introduced into urine, a faint luminescence is produced, which is greatly increased by the addition of a strong, alkaline solution of hydrogen peroxide. Potassium formate and formaldehyde produce the same effect as potassium cyanide. If Witte's peptone is hydrolysed by boiling it with alkali in an atmosphere of hydrogen, and strong alkaline hydrogen peroxide is added, a faint light is emitted. If formaldehyde is introduced before adding the hydrogen peroxide, a much more intense light of a pale green colour is produced. Glue gives a faint luminescence when treated in the same way, but egg-albumin, casein, glutenin, leucine, asparagine, glutamic acid, nucleic acids, and phytin give negative results. These experiments support the view that in living organisms the emission of light is due to the oxidation of a waste-product.

E. G.

Production of Fluorescent Radiation. J. CROSBY CHAPMAN (*Phil. Mag.*, 1913, [vi], 25, 870).—Polemical, in answer to Bragg's criticism (this vol., ii, 373).

J. F. S.

Chemical Production of Light. WILDER D. BANCROFT (*J. Franklin Inst.*, 1913, 175, 129—152).—The author discusses and classifies different forms of luminescence with the action of cathode rays on numerous oxides and salts and the probable influence of the acidic and basic ions contained on the colours of the light emitted. He considers that if the reaction velocity is sufficiently high, light will always be emitted, and that in describing this phenomenon the spectrum of a reaction should be spoken of, and not that of a substance.

F. M. G. M.

Uni-, Bi-, and Ter-valent Lines of Albumin in the Canal-Ray Spectrum (JOHANNES STARK, R. KÖNZER, and GEORG WEXDT (*Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 430—441. Compare this vol., ii, 172, 360).—It is shown that aluminium furnishes uni-, bi-, and ter-valent positive ions in the canal rays, and consequently gives canal-rays of three velocity intervals. With a fall of potential at the cathode of less than 8000 volts, the uni- and bi-valent aluminium ions are present in canal-rays in far larger numbers than the tervalent ions, but with a potential fall of over 8000 volts measurable numbers of tervalent aluminium ions are present. The uni-, bi-, and ter-valent aluminium ions are the carriers of different spectral lines. Thus, for example, the doublet $\lambda 3961.7$ — 3944.2 \AA is due to the univalent aluminium ions, the line $\lambda 4663.5 \text{ \AA}$ is due to the bivalent aluminium ions, and the lines $\lambda 4529.7$, 4513.0 , and 4480.0 \AA to the tervalent aluminium ions.

J. F. S.

The Purification and Concentration of Crude Radium-Barium Chlorides by Fractional Precipitation with Hydrochloric Acid. ERICH EBELER and W. BENDER (*Ber.*, 1913, 46, 1571—1573).—The method used is based on the practical insolubility of barium chloride in approx. 10*N*-hydrochloric acid (Ebeler, A., 1909, ii, 347). Soddy ("Chemistry of the Radioelements") has

pointed out that radium is carried down with the barium in the precipitation.

The authors find that when an aqueous solution of radium barium chloride is fractionally precipitated by leading into it hydrogen chloride gas, the first fractions are richer in radium than the salt started with; moreover, practically all the radium is precipitated with the first two-thirds of the barium chloride.

The above gives a much simpler fractionation method than that usually employed, since all the salts used are soluble in water.

T. S. P.

Occluded Gases and Radium and Uranium Contained in the Radioactive Tufa of Fiuggi. C. PORLEZZA and G. NORZI (*Gazzetta*, 1913, 43, i, 504—510. Compare Nasini and Levi, A., 1908, ii, 401).—The rock contains only very minute traces of helium. The quantity of radium per gram (measured by Strutt's method) is 5×10^{-12} , whilst the uranium amounts to 0.76×10^{-5} per gram of rock.

R. V. S.

Concentration of the Radioactive Emanation of the Gas of the Boraciferous "Soffioni" by means of Carbon at a Low Temperature. C. PORLEZZA and G. NORZI (*Gazzetta*, 1913, 43, i, 510—514).—When the gas from the "soffioni" of Larderello is passed over charcoal at -77° , it becomes inactive, and on heating the charcoal a gas is obtained from it which is thirty-four times more active (activity 6.8×10^6 volt-hour) than the natural gas.

R. V. S.

The Constancy of the Potassium Activity. WILHELM BILTZ and E. MARCUS (*Z. phys. anorg. Chem.*, 1913, 81, 369—377).—The examination of potassium salts from a large variety of natural minerals shows that the β -ray activity of potassium is very closely a constant, and the activity of the minerals is, within wide limits of the potassium content, proportional to that content. The evidence is against the assumption of an unknown active alkali-metal.

The minerals examined are: carnallite and sylvite from the Stassfurt deposits; orthoclase, muscovite, lepidolite, leucite, spodumene, and beryl, specimens of different origin being available in several cases. The Stassfurt minerals are converted into perchlorate, purified by recrystallisation, and then converted into sulphate. The silicates are either decomposed by hydrofluoric acid or by means of calcium carbonate and ammonium chloride, the latter method giving the better yield. The presence of lithium, rubidium, and caesium has been detected in several of the minerals, and an approximate estimation has been made in the case of Norwegian beryl.

C. H. D.

Ionisation in Gases and Gasous Mixtures by Röntgen and Corpuscular (Electronic) Radiations. CHARLES G. BARKLA and A. J. PHILIPOT (*Phil. Mag.*, 1913, [vi], 25, 832—856).—The

relative ionisations of air, hydrogen, nitrogen, oxygen, carbon dioxide, hydrogen sulphide, sulphur dioxide, ethyl bromide vapour, and methyl iodide vapour, by the complete absorption of corpuscular radiations set free by *X*-radiations have been determined by the authors. It is shown that there is no change in the relative ionisation with the velocity of the ionising corpuscles. The relative ionisations due to complete absorption of the corpuscular radiation are found to agree closely with the relative ionisations brought about by complete absorption of Röntgen radiation and its secondary radiations. The results indicate that the complete adsorption of a given *X*-radiation by different gases causes the emission of the same number of corpuscles. The ionisation coefficients for homogeneous *X*-radiations in a number of gases and vapours are determined, and the general laws stated by Barkla are confirmed. The ionisations in various gaseous and vapour mixtures due to complete absorption of corpuscular radiation are determined, and the values indicate that in the air-ethyl bromide mixture the relative absorptions of energy were very closely in agreement with the relative masses of the constituent gases. The ionisation by *X*-rays of gaseous mixtures has been shown to differ considerably from the sum of the ionisations of the constituent gases. The difference shows the effect of corpuscles from one gas being absorbed by the other, the general nature of the deviation being such as could be inferred from earlier experiments, although the amount of the difference is less than was to be expected on the theory of ionisation by ejected corpuscles. J. F. S.

Collisions between Gas Molecules and Slow Moving Electrons. J. FRANCK and GUSTAVE HERTZ (*Ber. Deut. physikal. Ges.*, 1913, 15, 373—390).—The paper deals with an investigation of the phenomena which occur when electrons collide with gas molecules at velocities at which they are unable to ionise the gas. It is shown that the free path of electrons, which are emitted with velocities corresponding with voltages between 2 and 10 volts, is of the order $4\sqrt{2}$ times the free path of the gas through which they are passing; this result is in agreement with the value previously found by Lenard. It appears therefore that at these velocities the electron-affinity and the electric charge have no noticeable influence on the free path. It is also shown that when electrons, moving at these velocities, collide with helium or hydrogen molecules, they are reflected with comparatively little loss of energy. From these results the authors put forward an hypothesis of the changes occurring at these collisions. They also state that at the reflection of electrons an energy change occurs between the molecule and the electron which does not take place in whole quanta as has been stated by Sommerfeld. J. F. S.

The Electronic Theory of the Metals. KARL F. HENZFELD (*Ann. Physik.* 1913, [iv], 41, 27—52).—A theoretical paper which starts from the hypothesis that in good conducting metals the transport of heat and electricity is brought about by the free

electrons alone. The various points considered are: (a) the calculation of the electron energy from the Wiedemann-Franz law; (b) calculation of the product of the number of electrons per c.c. and the free path ($n\lambda$) from the electro-conductivity; (c) calculation of the relationship of temperature and number of electrons from the Thomson effect; (d) the relationship between temperature and the free path of the electrons. It is shown in the paper that for good conducting metals the ratio $\alpha/\sigma T$ can be expressed by the formula $\alpha/\sigma T = 0.07244 \cdot 4N^2 \cdot dE/dT \cdot E/T$, in which T is the absolute temperature, E the energy of the electrons, N the number of atoms per gram molecule, σ the electrical conductivity, α the thermal conductivity. The value of E in the above equation is replaced by $E = \frac{1}{2} h\nu / e^{h\nu/kT} - 1$, in which e is the charge of the electron, and $h\nu/k$ for copper is 57.77, for aluminium, 104.5, for silver, 41, and for zinc, 28. From the Thomson effect, the relationship between n , the number of electrons in 1 c.c. of metal, and the temperature is given by the equation: $(n/n_0)^A = T e^{-q_0/T}$. For copper the values are $\alpha = 0.9711$ and $q_0 = 34.05$, and for aluminium, $\alpha = 1.001$ and $q_0 = 55.4$. From a discussion of the formula, the value of A is shown to be approximately $2/3$. It is also shown that Lindemann's formula, $1/\lambda = (B\sqrt{E} + C)^2$, does not represent the relationship between the free path and the temperature.

J. F. S.

Radioactivity of Some Minerals and Rocks. EMIL F. BELLMER (*Jahrb. Min.*, 1913, i, Ref. 184; from Pamphlet, *Freiburg, Schweiz*, 1911, 49 pp.).—Attempts were made to separate the various radioactive substances by a new method. In the case of orthite, the radioactivity is due solely to the small amount of thorium present. This mineral is widely distributed in the granites and gneisses of the Black Forest, and its presence accounts for the radioactivity of these rocks. Granites and other igneous rocks from Sumatra, Baden, and elsewhere were found to contain from $5 \cdot 10^{-6}$ to $6 \cdot 10^{-4}$ grams of thorium per gram of the rock. The radioactivity of samarskite is due to the presence of uranium, thorium, radium, and mesothorium-II.

L. J. S.

Electrical Conductivity of Some Pure Liquids: Ammonia, Acetone, Methyl and Ethyl Alcohol. JACQUES CARVALLO (*Compt. rend.*, 1913, 156, 1755—1758. Compare A., 1910, ii, 1026; 1912, ii, 119).—The author has determined the electrical conductivity of chemically pure specimens of these substances, when submitted to an electric current, a constant potential difference being maintained between the cell electrodes, with a view to determining the purifying effect and the apparent specific conductivity of the pure liquids. His results show that the prolonged passage of a current, through a liquid which is a bad conductor, leads to a conductivity limit, which may, according to the conditions and for the same liquid, be greater or less than the original conductivity. This method of purification does not apply to the two alcohols. W. G.

Electrical Resistance of a Few Metals Through a Wide Range of Temperature. EDWIN F. NORTHRUP and V. A. SUYDAM (*J. Franklin Inst.*, 1913, 175, 153—161).—A preliminary account of work undertaken for the purpose of perfecting a method whereby the electrical resistance of metals and alloys can be measured with ease, precision, and rapidity through a range of temperature between that of liquid air and a point a little below the boiling point of the substance in question; the same method is stated to be applicable to the case of molten salts.

To obtain data from which the relationship of resistance to temperature for metals, alloys, and molten salts which boil below 1500° can be expressed in curves, the following substances have been investigated by this method: mercury, lead, cadmium, zinc, tin, bismuth, and antimony, and their resistance in microhms per cm.-cube at various temperatures are tabulated. F. M. G. M.

Electrical Dispersion in Benzene, Toluene, and Petroleum. N. LINNITSCHENKO (*Physikal. Zeitsch.*, 1913, 14, 543—555).—The author has examined the dispersion and dielectric constants of benzene, toluene, and petroleum by three methods, which are modifications of the Drude method. It is shown that in the region of half wave-length 330—350 mm., there are no dispersion bands in benzene, toluene, or petroleum. The bands found by Colley (*A.*, 1908, ii, 909) and Obolenski (*A.*, 1910, ii, 562) are shown to have arisen from experimental errors. It is shown that the so-called methyl bands, which were supposed to be characteristic of the methyl group, have no existence. J. F. S.

Silicon and Its Position in the Thermoelectric Series. FRANZ FISCHER, RICHARD LEPSIUS, and ERNST BAERWIND (*Zeitsch. anorg. Chem.*, 1913, 81, 243—256. Compare Koenigsberger and Weiss, *A.*, 1911, ii, 578).—An apparatus is described by means of which irregular pieces of commercial silicon may be clamped between two masses of copper, one of which is heated and the other cooled. Some specimens of silicon are positive to copper, and others as strongly negative, and a thermo-couple composed of the two varieties may have a thermo-E.M.F. as high as 820 microvolts per 1°. The two varieties do not differ characteristically in electrical conductivity. The difference is due to the presence of silica. Melting silicon in contact with magnesia, lime, or alumina renders it positive, silica being removed. On the other hand, melting silicon so that a part of it burns and the oxide thus formed dissolves renders it negative. Several methods of bringing about the conversion are described. C. H. D.

Disturbing Influence of Air in Observations on the Concentration Cell. CHARLES M. VAN DEVENTER (*Chem. Weekblad*, 1913, 10, 472—477).—In a concentration cell with zinc and zinc sulphate, exclusion of air prevents change of polarity on dilution of the second liquid, and the E.M.F. of the cell corresponds with

that indicated by theory. If air is not excluded, accuracy of observation is impossible. A. J. W.

Electromotive Force of Silver Nitrate Concentration Cells. JAMES M. BELL and ALEXANDER L. FEILD (*J. Amer. Chem. Soc.*, 1913, 35, 715—718).—Measurements of the *E.M.F.* of concentration cells containing silver nitrate in aqueous and in alcoholic solutions have been made at 25° over a wider range of concentrations than have been used previously.

Determinations made with aqueous solutions accord with Nernst's formula for dilute solutions, $E = (2v/u + v)(RT/nF)\log_e c_1/c_2$, where c_1 and c_2 denote the concentration of the silver ions, and u and v the migration ratios of Ag^+ and NO_3^- . In the case of higher concentrations, however, the calculated value of the *E.M.F.* is greater than the observed value, since the migration ratio v is smaller at such concentrations. This affects the factor $2v/u + v$, and also affects the factor $\log_e c_1/c_2$, because the ratio c_1/c_2 is determined from conductivity measurements, and this method of determination is only valid when the migration velocity remains constant. The calculated value of the migration ratio for dilute solutions agrees closely with that found experimentally.

In the case of alcoholic solutions, the migration ratio seems to vary even at concentrations below 0.1*N*. The value of v calculated from the most dilute solution was 0.62. E. G.

The Nature of Overvoltage. JOHN I. CRABTREE (*J. Soc. Chem. Ind.*, 1913, 32, 521).—A statement of what is usually meant by overvoltage, and a discussion of its applications. T. S. P.

The Influence of the Addition of Colloids on the Anode and Cathode Reactions in the Electrolysis of Metal Salt Solutions (Lead and Zinc). I. ROBERT MARC (*Zeitsch. Elektrochem.*, 1913, 19, 431—444).—The influence of the addition of small quantities of gum arabic, starch, albumin, and gelatin on the nature of the cathode and anode products of the electrolysis of solutions of the following salts of lead is examined: acetate, silicofluoride, formate, benzoate, and salicylate, and of acetate, and silicofluoride, of zinc. It is shown all additions produce a finer grained deposit on the cathode, but that there is no relationship between the tendency to produce fine-grained deposits and the tendency to give coherent deposits. In many cases it is shown that the contrary is the case, and that with high current densities the coherence is much reduced by the addition of a colloid, whilst the size of the particles remains the same. The process depends evidently on two actions detrimental to one another. A coherent layer has a large plasticity and small particles as necessary conditions. From a pure solution the plasticity is at its maximum, as also is the tendency to form large crystals. With electrolytes which have great tendency to form large crystals, so much of a colloid must be added that the brittleness of the deposit naturally becomes too great of a coherent layer. It is shown that only

in special circumstances can a beneficial action of colloid additions be possible, and that colloids which are only slightly adsorbed by the deposit are more likely to have a favourable effect on the deposit than strongly adsorbed colloids. The author observed that lead crystals obtained by electrolysis showed Brownian movement up to crystals 15μ long and 2μ broad in colloid solutions, but not in pure water. He made experiments with barium and strontium carbonates and with barium sulphate, and found in these cases that the Brownian movement persists longer, and occurs with larger crystals (up to 0.5μ — 1μ) in a dilute solution of a colloid than in pure water. The reasons for the increased Brownian movement in colloidal solutions are stated to be that the presence of the colloid diminishes the adsorption by the glass of the solid particles. The excessive size of the lead crystals is explained by the fact that they are extremely thin; in some cases they are stated by the author to be transparent. The influence of the colloid on the cathode in addition to a change in the nature of the deposit is always hydrogen production, whilst on the anode several actions take place, among which the author notes formation of lead peroxide, evolution of oxygen, and formation of crusts of insoluble organic lead compounds. The last action is observed in the case of lead benzoate and salicylate, but the compounds have not yet been identified. Microphotographs of the various lead and zinc deposits are appended to the paper.

J. F. S.

The Coefficient of Magnetisation of Water and Oxygen. AUGUSTE PICCARD (*Arch. Sci. phys. nat.*, 1913, [iv], 35, 458—482. Compare this vol., ii, 473).—A detailed account of work published previously (this vol., ii, 17, 100). The values given, however, are slightly different. At 20° the coefficient of magnetisation and the susceptibility of water are respectively -0.7193×10^{-6} and -0.7180×10^{-6} , the temperature-coefficient of magnetisation being $+0.00012$. The susceptibility shows a flat maximum between 10° and 20° . The susceptibility of oxygen at 20° and 760 mm. is $+0.14073 \times 10^{-6}$; there are 7 magnetons to the atom of oxygen.

T. S. P.

The Magnetism of Aluminium Bronze. ROBERT C. GRAY (*Proc. Roy. Phil. Soc., Glasgow*, 1911—12, 43, 104—106).—The α -solid solutions of aluminium in copper become more retentive on quenching from 900° , whilst alloys containing the compound Cu_3Al become less retentive under the same treatment, in this respect resembling the Heusler alloys.

C. H. D.

Relation Between the Magnetic Field and the Passive State of Iron. III. HORACE G. BYERS and SETH C. LANGDON (*J. Amer. Chem. Soc.*, 1913, 35, 759—767).—Byers and Darrin (A., 1910, ii, 579) and Byers and Morgan (A., 1911, ii, 1057) have shown that when iron or nickel is used as an anode in certain electrolytes, the current density required to produce passivity is increased if the apparatus is placed in a magnetic field. It is now shown that

this retardation of the establishment of passivity is due to agitation of the electrolytes caused by the magnetic field, and that the same effect can be produced by mechanical stirring or by rotation of the anode. No satisfactory explanation of this effect of stirring can be offered.

E. G.

Some Physical Properties of Alloys of Iron and Copper.
ALEXANDER D. ROSS (*Proc. Roy. Phil. Soc. Glasgow*, 1911-12, **43**, 62-66).—The magnetic properties of iron deteriorate with increasing copper up to 0.15%, the hysteresis loss increasing. Beyond this, the quality improves up to 0.4%, at which composition the alloy is almost equal to standard iron. Higher proportions of copper again diminish the susceptibility. The difference between the Ar_2 and Ac_2 points is greater in these alloys than in pure iron.

C. H. D.

The Magneto-chemistry of Some Ferric Salts and the Theory of the Magneton. B. CABRERA and ENRIQUE MOLES (*Arch. Sci. phys. nat.*, 1913, [iv], **35**, 425-457; *Anal. Fis. Quim.*, 1912, **10**, 394).—The measurements of the coefficient of magnetisation were carried out according to the method given by Piccard (this vol., ii, 17).

The results obtained for the specific susceptibilities of solutions of ferric chloride, ferric nitrate, and sodium ferric pyrophosphate give a value for the atomic susceptibility of iron which varies with the concentration. This variation is probably due to changes which take place in the dissolved salt, as, for example, dissociation and hydrolysis, and consequently it is impossible to draw conclusions from measurements made with one concentration only, as has been done previously by some investigators.

When the number of magnetons is calculated for infinite dilution the law of whole numbers put forward by Weiss is confirmed, these numbers being either 25 or 27 for the compounds mentioned above. In the case of ferric chloride, which was the only substance which could be investigated in very concentrated solutions, the number of magnetons tends to approach the value 29 for the most concentrated solutions, which value is the same as that obtained by Feytis for sublimed ferric chloride. The curve for ferric nitrate, showing the relation between the number of magnetons and the concentration, also tends to the same value at high concentrations. The solutions of sodium ferric pyrophosphate are somewhat unstable and viscous, but the limiting value for high concentrations is apparently 27. It follows that the number of magnetons for the atom of iron is always 25, 27, or 29.

A study has also been made of the influence of the addition of the corresponding acid, or of salts with the same anion, to the above ferric salts. The results indicate that hydron and anion exert separate influences; the hydron tends to restore the molecule to its original condition, the number of magnetons approaching 29, whilst the anion apparently increases the susceptibility in a continuous manner.

T. S. P.

Magnetic Study of the Constitution of Some Alloys of Antimony. P. LEROUX (*Compt. rend.*, 1913, 156, 1764—1766).—The author has determined the specific coefficients of magnetisation of alloys of antimony-tin and antimony-lead, and curves are given showing the variations of these coefficients with the composition of the alloys. The results are in agreement with those obtained by Pouchine (*Rev. Metallurgie*, 1907, 4, 933) from the measurements of the *E.M.F.* of these alloys, and point to the existence of an antimony-tin compound containing 50% antimony. There is a second angular point at 95% antimony corresponding perhaps with a limit solid solution. The alloys antimony-lead are more complicated, and the existence of a compound containing 85—86% antimony is probable. W. G.

Relationship of the Coefficient of Expansion and the Coefficient of Compressibility of Water Vapour to Pressure and Temperature. ÉMILE WERTHEIMER (*Zeitsch. physikal. Chem.*, 1913, 83, 260—268).—A mathematical paper, in which the above-mentioned relationships are considered. It is shown that over the temperature interval 96—220° the coefficient of expansion at constant temperature increases with the pressure, and at constant pressure decreases with increasing temperature. It approaches the ideal value with increasing superheating. The maximum divergence from the ideal value, in the region considered, amounts to 30%. With regard to the coefficient of compressibility, it is shown that the divergence from the ideal value increases with increasing pressure at constant temperature, and decreases with increasing temperature at constant pressure. The maximum divergence amounts to 7% in the region considered. The equations deduced for water vapour are shown to hold generally for saturated vapours. J. F. S.

Improvement in Gas Thermo-Regulators. A. WHITAKER (*Chem. News*, 1913, 107, 242—243).—The improvement consists in a modification of the gas inlet and the mercury outlet tubes, which ensures that the mercury seals by entering the comparatively narrow orifice of the inlet tube. The end of the inlet tube is ground internally to form a cone, the edges of which are either sharp or slightly expanded. This is brought close up to the end of the capillary outlet tube, which is countersunk by grinding, so as to present an obtuse and symmetrical aperture. With this arrangement there is no danger of external sealing. H. M. D.

Comparison of the Optical and Thermal Methods for the Determination of Melting Points. RICHARD NACKEN (*Centr. Min.*, 1913, 328—337).—The optical method used consists in the observation of a thin plate of the substance between crossed nicols. The substance is heated in a horizontal electric furnace, the ends of the inner tube of which are closed by quartz; the temperature is measured by means of a thermocouple. The melting point is taken as the temperature at which the substance loses the optical

properties of a crystal, as indicated by examination between the nicols.

Experiments with anorthite, albite, adular, and sanidine showed that the optical and thermal methods gave results which agreed satisfactorily. Former differences which have been found are considered to be due to errors inherent in the optical methods used; for example, the disappearance of the sharp edges of a crystal is a very unsatisfactory sign of melting.

T. S. P.

Behaviour of Solids Under Unevenly Distributed Pressure.
HENDRIK E. BOEKE (*Centr. Min.*, 1913, 321—324).—Johnston's theory (*A.*, 1912, ii, 129; this vol., ii, 290) is discussed with a view to inciting further experimental work on the subject. T. S. P.

Matter in the Superfused State and the Discontinuity in Some of its Physical Properties in the Neighbourhood of the Melting Point. RAFFAELE NASINI and U. BRESCIANI (*Mem. R. Accad. Lincei.*, 1913, [v], 9, 341—401).—The authors have studied the rate of cooling of a considerable number of superfused substances, and from the results they have constructed not only the ordinary curves in which the abscissae are times and the ordinates temperatures, but also differential curves, in which the abscissae are temperatures and the ordinates are the differences between the times taken for the mercury to fall 0.1° at these temperatures (respectively) and the time it takes to fall 0.1° at the beginning of the cooling. The latter curves show a discontinuity, corresponding with a diminution in the rate of cooling, in the neighbourhood of the melting point of the substance. This phenomenon the authors propose to name the "Moreschini effect" (compare Moreschini, *A.*, 1900, ii, 465). The effect is pronounced only in some cases, but slight anomaly is almost always to be observed. In the case of the substances which exhibit the phenomenon best, the contraction in volume during the cooling was determined, and the changes in volume were measured pyknometrically, but no corresponding peculiarity was observable with certainty. It was found, however, that these substances show a maximum specific heat at the corresponding temperature, and they also show, to a greater or lesser degree, peculiarities in the value of the surface tension about the melting point.

The experimental results are given in a large number of tables and curves. Among the substances showing the effect most are thymol, anethole, acetic acid, and palmitic acid. The observations of the rate of cooling were carried out with the aid of an apparatus similar to that of Beckmann for measuring depression of the melting point, but it was provided with a mechanical stirrer, and with an arrangement to ensure a dry atmosphere in contact with the superfused substance. The rate of cooling was measured with the aid of a stop-watch for each alternate interval of 0.1° . The specific heats were determined by means of Pfaundler's apparatus, and the surface tension with that of Ramsay and Shields.

R. V. S.

Calculation of Latent Heats of Vaporisation. L. GAY (*Compt. rend.*, 1913, 156, 1464—1466).—The author modifies Clapeyron's formula $(v_1 - v_2)dP = ELdT/T$, where v_1 and v_2 are the molecular volumes of the vapour and liquid respectively, to $(Pv_1/RT - Pv_2/RT)d\log P = ELdT/RT^2$, and determines the values of $(Pv_1/RT - Pv_2/RT)$ in terms of the reduced pressure P/π according to Amagat (this vol., ii, 188). This he has done in the case of fluorobenzene, isopentane, stannic chloride, and methyl alcohol, using the physical constants given by different workers.

W. G.

The Temperature of Sublimation. JOHN JOLY (*Phil. Mag.*, 1913, [vi], 25, 856—869; *Chem. News*, 1913, 107, 241—242).—The author has determined the temperatures at which sublimation occurs when various finely powdered minerals containing arsenic, antimony, and tellurium are heated in contact with the air. From the results obtained with the minerals containing arsenic, it would appear that the sublimation of the arsenic is definitely related to the structure, the various minerals falling into groups which are characterised by very different sublimation temperatures. This behaviour is also shown by the tellurides, whereas the antimony-containing minerals of the type nRS, mSb_2S_3 are found to sublime over a range of temperature which is but little influenced by R , n or m .

H. M. D.

Trouton's Ratio. ROBERT DE FORCRAND (*Compt. rend.*, 1913, 156, 1439—1443).—A theoretical paper in which the author advocates a further modification of Nernst's revision of Trouton's law, in order to account for the values found for substances, such as zinc, lead, copper, silver, boiling at above 1000° absolute. The new equation given is:

$$L/T = 10.1 \log T - 1.5 - 0.009T + 0.000026T^2. \quad \text{W. G.}$$

Trouton's Ratio and the Molecular Heat of Vaporisation of Pure Substances Boiling at High Temperatures. ROBERT DE FORCRAND (*Compt. rend.*, 1913, 156, 1648—1651).—A theoretical paper, in which the author gives further evidence in support of his equation modifying Trouton's law (compare preceding abstract).

W. G.

New Formulæ for Representing the Vapour Pressure of Water Vapour. II. P. H. HOFBAUER (*Zeitsch. physikal. Chem.*, 1913, 83, 336—338. Compare A., 1912, ii, 735).—A mathematical paper, in which additions are made to the formulæ already quoted (*loc. cit.*), and instances quoted to confirm the formulæ.

J. F. S.

A Law of Tonometry and its Consequences Relative to the Ionic Theory. EUGÈNE FOUARD (*Compt. rend.*, 1913, 156, 1761—1763).—A theoretical paper, in which the author deduces that for each solvent at a temperature T , between 0° and 25° , the molecular diminution of the vapour tensions of its solutions tends,

as the dilution increases indefinitely, towards a limit value, represented by the physical molecular weight, M_r , of the liquid solvent. Further, that the degree of electrolytic dissociation of a normal solution of a substance, such as potassium chloride, when determined by the tonometric method of Raoult-Arrhenius, varies with the temperature in an absolutely discordant manner, not shown by electrical conductivity measurements. W. G.

The Law of Volatility in Chemical Reactions. CAMILLE MATIGNON (*Compt. rend.*, 1913, 156, 1536–1538).—Berthollet's law with regard to the reaction of non-volatile substances (compare *La Statique Chimique*) is capable of generalisation. All systems of non-volatile solid or liquid substances capable of giving rise, by a new grouping of the atoms, to a system containing volatile substances must enter into reaction at a suitable temperature. This has recently found application in the reduction of magnesium oxide by aluminium (compare this vol., ii, 505), and the reduction of barium oxide by silicon (compare this vol., ii, 504). It also explains the reducing action of carbon. The law can be further extended to systems containing volatile substances. A reaction which contains volatile substances in its initial and final systems is facilitated when the volatile molecules are more numerous in the final than in the initial system. W. G.

New Thermodynamical Results from the Theory of Quanta. MICHAEL POLÁNYI (*Zeitsch. physikal. Chem.*, 1913, 83, 339–369).—A theoretical paper, in which the entropy relationships for various systems are mathematically considered. J. F. S.

Precision Viscometer for the Measurement of Relative Viscosity, and the Relative Viscosities of Water at 0°, 18°, 25°, and 50°. EDWARD W. WASHBURN and GUY Y. WILLIAMS (*J. Amer. Chem. Soc.*, 1913, 35, 737–749).—With a view to undertake a comprehensive study of the relation between the conductivities of ions and the viscosity of the medium in aqueous solutions, an effort has been made to improve the Ostwald type of viscometer, so as to render it more convenient and more accurate.

An improved apparatus is described which is made of fused quartz, and possesses the following advantages. Its water-constant at a given temperature is not changed by cleaning it with hot liquids or subjecting it to large variations of temperature. The water-constant at 25° is 580 seconds, and is reproducible to about 0.03 second under given conditions, so that a precision of at least 0.01% is attainable in measurements of relative viscosity. For effective pressures between 130 and 300 mm. of water, the deviation from the requirements of Poiseuille's law is less than 0.03%. An error of 1 c.c. in the liquid introduced into the viscometer does not change the time of flow by as much as 0.05%. A single instrument can be used for a large range of temperature, as its dimensions do not change with the temperature.

The relative viscosity of water at different temperatures was found to be:

$$\eta_{18^\circ}/\eta_0 = 0.58978; \eta_{20^\circ}/\eta_0 = 0.49741; \eta_{25^\circ}/\eta_0 = 0.30640; \eta_{30^\circ}/\eta_{25^\circ} = 0.61599.$$

The relative viscosity of *N*-potassium chloride at 18° is 0.98130.

E. G.

Importance of Viscosity for the Study of the Colloidal State. WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 213—222).—A general theoretical paper, giving a résumé of the factors which govern the viscosity of colloids and the various facts which may be deduced from viscosimetric measurements. It is shown that in a colloidal system the viscosity is affected by ten variables, namely, concentration, temperature, dispersity, solvate formation, electric charge, previous thermal treatment, previous mechanical treatment, inoculation with small quantities of more viscous colloids, time (that is, age of the colloids), and additions of both electrolytes and non-electrolytes. The measurement of viscosity is shown also to be a good method of determining the points at which "changes of state" occur; among the changes of state for which it has been used the author mentions, changes in dispersity, solvate formation, peptisation, coagulation, gelatinisation, and imbibition. Each of these changes is discussed for special cases. It is also pointed out that viscosity measurements would afford valuable evidence in many industrial problems, for example, in the case of caoutchouc sols. In this case the "nerve" of caoutchouc corresponds with a higher viscosity of its solutions; "killed" or depolymerised caoutchouc, which has been rendered less elastic, gives lower viscosities at the same concentrations than caoutchouc which has not been treated mechanically. J. F. S.

The Viscosity and Electrochemistry of Protein Solutions. WOLFGANG PAULI (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 222—230).—The paper deals with the relationships between the viscosity and the electrochemical properties of colloids. For this consideration it is divided into two parts: 1, which deals with the relationships at the isoelectric point, that is, the point at which the acid and basic ionisations of the proteins are identical, and 2, the relationship after the isoelectric point has been passed. It is shown that the isoelectric point is independent of the protein concentration, and that the swelling of gluten is a minimum at this point. Further, the coagulation of albumin solutions by alcohol has its maximum at the isoelectric point. The isoelectric point corresponds exactly with a maximum of dehydration and a minimum of viscosity for albumin solutions. As soon as the isoelectric point is passed by driving back the concentration of hydrogen ions by means of acid, it is shown that the hydrogen ions become fixed up to a certain concentration of acid, but that the chlorine ions only become fixed beyond this concentration. The viscosity of acid albumin is shown to rise to a maximum with increase of acid, which then falls off as the acid becomes excessive. In connexion with these relationships, the work of a large number of investigators is examined. It is shown finally that by viscosity measurements it has been pos-

sible to indicate the formation of an albumin caffeine hydrochloride complex, which is characterised by a greater hydration than the albumin chloride itself. The effect observed is a rapid increase of the viscosity with the addition of caffeine up to a maximum, after which the viscosity decreases. This result has only been observed for albumin, and is not given by gluten or fibrin or the direct decomposition products of albumin.

J. F. S.

General Theory of Viscosity of Two-Phase Systems. EMIL HATSCHER (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 238—248).—The general theory of two-phase colloidal systems put forward by the author (A., 1911, ii, 19, 98) is discussed, and the formula obtained by him, $\eta' = \eta(1 + 4.5f)$, compared with the formula of Einstein (*Ann. Physik*, 1906, [iv], 19, 289), $\eta' = \eta(1 + f)$. These formulæ are examined in connexion with viscosity measurements made by various observers on suspensoids. The question of the effective volume of the disperse phase is considered, and it is shown that it is the sum of two factors, the volume of the actual disperse phase (probably but not necessarily proportional to the weight), and the volume of the adsorption envelope. The authors, using figures obtained by Odén for sulphur sols (A., 1912, ii, 1143), calculate that the thickness of this layer is 0.87μ . It is shown that with two-phase colloids it is advantageous to study the viscosity changes by a method which allows of a varying "rate of shear." This is not possible with the Ostwald viscometer, where the rate of shear is determined by the diameter of the capillary and the density of the liquid, but is possible by means of Couette's apparatus, which is described. A few preliminary measurements are given for a paraffin soap solution emulsion.

J. F. S.

Viscosities and Conductivities of Aqueous Solutions of Raffinose. EDWARD W. WASHBURN and GUY Y. WILLIAMS (*J. Amer. Chem. Soc.*, 1913, 35, 750—754).—In continuation of the investigation of the relation between ion conductivities and the viscosity of the medium (A., 1911, ii, 862), raffinose has been selected as the first non-electrolyte to be employed for changing the viscosity.

An account is given of a method of preparing pure raffinose, and the conductivities at 0° and 25° , and the densities and relative viscosities at 0° , 25° , and 50° , of its aqueous solutions of various concentrations are recorded.

E. G.

Experiments on Wetting, and on the Adhesion of Solid Particles at the Surface of Two Liquids. F. B. HOFMANN (*Zeitsch. physikal. Chem.*, 1913, 83, 385—423. Compare Stark, *Ann. Phys. Chem.*, 1898, [iii], 65, 287; Pickering, T., 1907, 91, 2001).—Experiments are described showing that when a fine powder is shaken with two liquids which are not completely miscible, the powder is entirely retained at the surface of contact of the two liquids. This action is shown to be due to the partial wetting of the particles by both liquids. The wetting of glass surfaces was studied in the case of a number of liquids and mixtures of liquids. It is shown in this case that the partial wetting of a glass

surface by a mixture of two liquids runs parallel with the adhesion of small glass particles at the surface of contact of the same two liquids. Experiments were then made with thin plate crystals and powders of a number of substances, and it is shown that in those cases where the thin crystal adheres strongly to the surface the powder also, on shaking with the liquid, will adhere to the surface; in those cases where the thin crystals adhere only slightly, a part only of the powder adheres to the surface; and finally, where the thin crystals do not adhere, neither does the powder. A table is given of the action of water and one of the following liquids on a number of inorganic substances: ether, chloroform, isobutyl alcohol, benzene, xylene, petroleum, isocamyl alcohol, and paraffin oil.

J. F. S.

Determination of the Surface Tension of Molten Lead in Contact with Molten Mixtures of Lead and Potassium Chlorides. (Theory of Metal Fog Formation.) RICHARD LORENZ and ALFRED LIEBMANN (*Zeitsch. physikal. Chem.*, 1913, 83, 459—480).—The authors have measured the surface tension of molten lead in contact with molten lead chloride, and mixtures of lead chloride and potassium chloride by the rise in capillary tubes. The capillary apparatus was of Jena glass and of the usual form; a quantity of pure lead was placed in the wider tube, and covered with a layer of a molecular mixture of potassium chloride and lead chloride to preserve it from oxidation. The apparatus was then sunk in a bath of molten lead chloride, so that the capillary tube was completely immersed, whilst the wider tube was open to the air. The heating was electric, and the temperature measurements were obtained by means of a platinum, platinum-rhodium thermocouple. The measurements fell into three groups: (1) the measurement of the surface tension of a molecular mixture of molten lead and potassium chlorides in contact with the air at temperatures 457—616°; (2) measurement of the surface tension of molten lead against the molecular mixture of lead chloride and potassium chloride at temperatures 605—448°; and (3) measurement of the surface tension of lead in contact with a series of potassium and lead chloride mixtures (varying from 100% PbCl_2 to 78.39% PbCl_2) at temperatures 555°, 508°, and 600°. The necessary density values were taken from the measurements of Lorenz, Frei, and Jabs (A., 1908, ii, 156). From the results it is shown that the theory of Lorenz and Kaufler (A., 1908, ii, 1023), which states that the surface tension of molten liquids, in contact with molten salts, changes, is in accord with facts. The surface tension of lead in contact with PbCl_2 increases at 600° by the addition of 16% KCl from 170.1 dyne/cm. to 203.4 dynes/cm. Temperature plays a considerable part in the increase; thus, at 600°, the increase in the case quoted is 12—14%, whilst at 550° it is 20%, and at 510°, 30%. The disappearance of metal fog by the addition of potassium chloride is similar to the disappearance of precipitates in colloidal solutions, although of a fundamentally different nature. It is shown that the fog formation of metal decreases with the increasing

surface tension as occasioned by the molten electrolyte in contact with the metal. This is explained on the assumption that the fog formation is due in some way to the solution pressure, inner pressure, and vapour pressure of the metal, and that the forces at work on the surface, that is, those which condition the surface tension, act against the internal forces.

J. F. S.

The Nature and Cause of Sorption from Aqueous Solutions.

GEORG VON GEORGIEVICS (*Zeitsch. physikal. Chem.*, 1913, 83, 269—279).—A theoretical paper, in which the results of previous papers (A., 1911, i, 537; ii, 1070; 1912, ii, 140, 236, and the following abstracts) are considered. It is shown that the x value of the expression for the partition relationships $\sqrt{c_1/c_2} = K$ runs parallel with the strength of the acid used, and consequently the adsorption is determined by the strength of the acid. Of two acids of equal strength, the one with the greater viscosity is more strongly absorbed by wool. Hence a large viscosity brings about a greater solubility of the acid in the adsorbent; so that it follows that the sorption (adsorption and solution) of acids in wool is determined by the strength of the acid and the viscosity. The usual method of considering adsorption as a concentration of the adsorbed material on the surface of the adsorbent is shown to be unsatisfactory, and it is shown that experiment indicates that a concentration of the adsorbed substance takes place on all the molecules of the adsorbent, as far as this is not rendered impossible by any hindrance of the diffusion. A hypothesis is put forward to show how the adsorption can pass over to chemical reaction between the adsorbed material and the adsorbent.

J. F. S.

Adsorption in Solutions. IV. The Significance of the x in the Distribution Formula and the Causes of Sorption. GEORG VON GEORGIEVICS (*Monatsh.*, 1913, 34, 733—749. Compare A., 1912, ii, 140, 236).—The interpretation of the meaning of x in the ordinary distribution formula, $\sqrt{c_1/c_2} = K$, has hitherto been a matter of difficulty. When the range of concentrations varies greatly it is often necessary to have different values of x for different ranges of concentration in order to obtain a constant value of K . In order to interpret the meaning of x , the author proceeds as follows. In any given series of concentrations, the value of x is calculated for each consecutive pair of concentrations; the mean of the various values of x is then taken for the series. It is then found that if a number of acids is arranged in the order of their strengths, then the mean values of x , calculated from experiments on the distribution of these acids between water and wool, also follow the same order. If the value of x were 1, no adsorption would take place, the acid merely dissolving in the adsorbent (wool); when, however, a hindrance to sorption (adsorption + solution) takes place, adsorption occurs to a greater or lesser extent, and the value of x increases. It follows that the stronger an acid is, the more it is adsorbed by wool, since the value of x increases with the strength of the acid.

Comparison of the values of x and the viscosity of the aqueous solutions of the various acids shows that within one and the same group of acids, that is, mineral acids, or fatty acids, etc., the adsorption is all the greater the smaller the viscosity. Acids, therefore, which have the smallest value of x are dissolved by the wool in the greatest proportion during the process of sorption.

Considerations such as the above lead the author to the conclusion that the strength of acids and the viscosity of their solutions are the two chief factors which regulate the whole process of sorption.

Apparently there is no relation between adsorption and surface tension. If, however, the acids are arranged in the order of descending values of x , that is, in the order of decreasing adsorption, the same order is obtained as for their toxic action towards bacilli; the reverse order is obtained for the hæmolytic action of these acids.

The distribution coefficient of the following acids* between water and wool was measured: formic, malonic, and adipic acids.

T. S. P.

Adsorption in Solutions. V. Solution, Adsorption, Chemical Combination, Adhesion. GEORG VON GEORGIEVICH (*Monatsh.*, 1913, 34, 751—757).—Arguments are adduced against the assumption that the process of sorption is essentially chemical. Various considerations, which depend to a great extent on those given in the previous abstract, lead the author to account for the process of sorption between wool and acid solutions as follows: The acid dissolved in the water diffuses into the wool fibre and distributes itself uniformly. As further diffusion takes place and the concentration of the sorbed substance in the adsorbent becomes greater, the chemical attraction of the molecules of the adsorbent comes into play, and adsorption, which consists in the gradually increasing accumulation of the sorbed substance round the individual molecules of the adsorbent, occurs. As the adsorption increases, the attraction of the molecules of the adsorbent for those in the sorption solution decreases, and consequently a retardation of the sorption occurs, which retardation is a characteristic sign of adsorption.

T. S. P.

The Determination of the Chlorine and Sulphur Trioxide Pressures in the Case of Chlorides and Sulphates. LOTHAR WÖHLER and M. GRÜNZWIG (*Ber.*, 1913, 43, 1587—1590).—The authors describe an improvement of the apparatus previously used by Wöhler and Plüddemann (*A.*, 1908, ii, 290) for the determination of the sulphur trioxide tension of sulphates, whereby the vapour tension of chlorides can also be determined.

With the new apparatus, the measurements on ferric sulphate gave results in agreement with those obtained by Bodenstein and Suzuki (*A.*, 1910, ii, 1042). The results obtained previously for cerous sulphate were confirmed, at all events for the higher temperatures, and a fresh calculation of the sulphur trioxide partial pressures given.

T. S. P.

Studies on Osmosis. C. FERDINAND NELSON (*J. Amer. Chem. Soc.*, 1913, 35, 658—671).—Kahlenberg (A., 1906, ii, 337) and Wilcox (A., 1910, ii, 693) have determined the osmotic pressures of solutions of certain substances in pyridine when separated from pure pyridine by a caoutchouc membrane. This work has now been extended.

It has been found that pyridine solutions of metallic abietates readily pass through the membrane without producing any considerable rise of liquid in the osmometer tube. The oleates, palmitates, and stearates, camphor, phenol, thymol, and benzoic acid all behave similarly. All these compounds are easily soluble in hydrocarbons, such as benzene and petroleum, and are therefore also soluble in caoutchouc and thus pass through the membrane. On the other hand, certain compounds also soluble in pyridine, such as silver thiocyanate, copper chloride, lead nitrate, copper formate, dextrose, lævulose, "saccharin," and hippuric acid, do not pass through the membrane so easily nor in such large quantities, and these are insoluble, or nearly so, in hydrocarbons. The effect of adding water in various amounts to the inner and outer liquids of an osmotic cell, either separately or simultaneously, has been determined for several compounds. Of the compounds examined with the object of determining their suitability for use in direct osmotic pressure measurements, lead nitrate and dextrose have been found to approximate most closely to sucrose and silver nitrate with regard to semi-permeability towards a caoutchouc membrane when pyridine is used as solvent.

The results support Kahlenberg's chemical theory of osmosis, according to which the phenomenon is selective and depends on the specific natures of the solvent, solute, and membrane, instead of being due to the purely physical factors of porosity, capillarity, and surface tension.

E. G.

Diffusion in Solids. CECIL H. DESCH (*Rep. Brit. Assoc.*, 1912, 348—372).—A summary of knowledge on this subject, arranged under the following heads: diffusion in glasses; devitrification; electrolysis of glass and porcelain; diffusion of gases through metals; passage of liquids through metals; solid diffusion in metals; cementation and decarburisation of iron; segregation and crystallisation; influence of the amorphous modification in metals; electrolysis of crystalline solids; diffusion in minerals, artificial crystals and colloidal gels, Liesegang's phenomenon. C. H. D.

Diffusion of an Electrolyte in Gelatin. L. WILLIAM ÖRÖLM (*Chem. Zentr.*, 1913, i, 1648; from *Med. Vetenskapsakad. Nobelinstitut.*, 1913, 2, 30, pp. 8).—The diffusion-coefficient of potassium chloride in gelatin solutions of different concentrations has been measured in a vessel composed of four superposed brass cylinders, the solution being placed in the bottom section and the solvent in the others, such a system being especially adapted to viscous solutions. The coefficient decreases with increasing concentration exactly like the conductivity, so that it can be calculated from measurements of

the latter. Gelatin therefore influences the ionic velocity, but not the degree of dissociation.

J. C. W.

The Dependence of Diffusion on the Viscosity of the Solvent. L. WILLIAM ÖHOLM (*Chem. Zentr.*, 1913, i, 1648—1649; from *Med. Vetenskapsakad. Nobelinstitut.*, 1913, 2, 26, pp. 21).—The diffusion-coefficients of glycerol and bromoform in ether, benzene, acetone, methyl, ethyl, propyl and amyl alcohols, and aqueous alcohol have been obtained, the concentrations being measured refractometrically. Except in the case of glycerol in amyl alcohol, the solutions are more viscous than the solvents. The percentage increment of the viscosity on the addition of the same quantity of glycerol is irregular for different solvents, but in the case of bromoform the increase is greater the smaller the initial viscosity. The diffusibility of glycerol decreases with increasing viscosity and concentration; $k\eta$ is about 0.46 in the case of methyl, ethyl and propyl alcohols, but varies widely between 50% alcohol and amyl alcohol. Glycerol is much less complex in alcoholic than in aqueous solution. The diffusibility of bromoform varies less with viscosity, but the values of $k\eta$ are irregular, decreasing with increasing molecular weight of the solvent. The product $k_{\infty} \sqrt{M}$ is greater for bromoform than for glycerol.

J. C. W.

Free Diffusion of Non-Electrolytes. II. Diffusion of Some Organic Substances in Water. L. WILLIAM ÖHOLM (*Chem. Zentr.*, 1913, i, 1649—1650; from *Med. Vetenskapsakad. Nobelinstitut.*, 1912, 2, 23, pp. 52. Compare A., 1910, ii, 273).—The diffusion-coefficients of a number of inactive substances have been measured, the concentrations being arrived at by refractometric means. The values rise with increasing dilution, but for different substances the variation is widely different, and the coefficients for solutions of equal concentration are very far apart. The temperature-coefficients of diffusion are about the same as in the former paper. The variations of the diffusion-coefficients at 20° for the extreme limits of concentration employed are as follows: glycerol, 0.645 to 0.717 for 2*N* to 0.125*N*; acetamide, 0.685 to 0.900 for 10*N* to 0.25*N*; carbamide, 0.986 to 1.022 for 2*N* to 0.25*N*; mannitol, 0.459 to 0.500 for 0.5*N* to 0.125*N*; quinol, 0.640 to 0.665 for 0.7*N* to 0.25*N*; resorcinol, 0.524 to 0.654 for 2*N* to 0.125*N*; alloxan, 0.531 to 0.570 for 1*N* to 0.125*N*; pentaerythritol, 0.573 to 0.589 for 0.4*N* to 0.2*N*; saligenin, 0.521 to 0.619 for 1*N* to 0.25*N*; eegonine, 0.528 to 0.604 for 1*N* to 0.1*N*; dicyanodiamide, 0.860 to 0.895 for 0.4*N* to 0.2*N*; salicin, 0.402 to 0.422 for 0.12*N* to 0.06*N*; caffeine, 0.488 for 0.05*N*; inulin, 0.132 to 0.138 for 0.01*N* to 0.005*N*; gum arabic, 0.193 to 0.203 for 4.9% to 2.4%; starch paste, 0.207 to 0.214 for 8% to 5%, and starch powder, 0.058 to 0.0676 for 4.98% to 1.23%.

The product $k_{\infty} \sqrt{M}$ is again about 7. From this expression the molecular weight of gum arabic must be about 1050, of starch paste, 970, and starch powder, 10,000. The diameter of the molecule has also been calculated, and is of the order 10^{-8} cm. for ordinary compounds, and 10^{-7} cm. for colloidal substances.

J. C. W.

Diffusion of Some Organic Substances in Ethyl Alcohol.

L. WILLIAM ÖHOLM (*Chem. Zentr.*, 1913, i, 1650—1651; from *Med. Vetenskapsakad. Nobelinstitut.*, 1912, 2, 24, pp. 34. Compare preceding abstract).—The diffusion of a large number of organic compounds in ethyl alcohol has been studied with analogous results. The diffusibility falls from 1.08 and 0.98 for chloroform and acetone to 0.60 for camphor, 0.25 for aconitine, and 0.16 for carminic acid, and rises on dilution as in aqueous solution. The product $k_{\infty} \sqrt{M}$ is about 4.4 for acetamide, glycerol, resorcinol, and quinol, but for saligenin, acetin, and eosin-sodium it is 5.7. Assuming that the diffusion-coefficient for the same substance and same concentration is proportional to the viscosity of the solvent, the constant, calculated from the value 7 for aqueous solutions, should be 5.24. This assumption is not always justified, however (see above), and some of the values obtained in the present instance, when recalculated for aqueous solutions, would become as much as 15.

J. C. W.

Solubility. II. J. VARGAS EYRE (*Rep. Brit. Assoc.*, 1912, 795—871).—The report deals with work on solubility published between 1895 and 1911, under the following headings: I, Introduction; II, Methods of Determination; III, Influence of Nature of Solvent; IV, Influence of Nature of Solute; V, Solubility in relation to (a) temperature, (b) pressure, (c) influence of other substances; VI, Mutual solubility and distribution coefficients; VII, Theoretical considerations; VIII, Chronological bibliography; IX, Authors' index.

C. H. D.

Dissociation Constant of Weak Acids and Bases from Solubility Data. NILRATAN DHAR (*J. Amer. Chem. Soc.*, 1913, 35, 800—802).—The solubility of an acid is increased in presence of the salt of a weak base and a strong acid, benzoic acid, for example, being more soluble in a solution of sodium acetate than in the same volume of water. It is shown that, assuming the dissociation constant of benzoic acid, the dissociation constant of acetic acid is given by the formula $(6 \times 10^{-5} \times a)(c - 6 + a)/(b - a)^2$, where a is the solubility of benzoic acid in water, and b its solubility in a solution of sodium acetate of concentration c . Philip (T., 1905, 37, 987) and Philip and Garner (T., 1909, 95, 1466) have determined the solubility of cinnamic, benzoic, salicylic, and nitrobenzoic acids in solutions of sodium acetate, sodium butyrate, sodium formate, sodium monochloroacetate, and sodium salicylate. Calculations have been made from these data, and fairly concordant results have been obtained with cinnamic and benzoic acids. Similar results are obtainable from the potassium salts. In the case of salicylic and nitrobenzoic acids, difficulty arises owing to ionisation, as these are fairly strong acids.

E. G.

Dissociation Constants of Monobasic Acids. NILRATAN DHAR and ASWINI KUMAR DATTA (*Zeitsch. Elektrochem.*, 1913, 19, 407—409).—Carbon dioxide is more soluble in solutions of sodium

salts of weak acids than it is in water. This fact is made the basis of a method of determining ionisation constants of weak acids. A small Erlenmeyer flask, containing about 100 c.c. of an aqueous solution of the sodium salt of a weak acid, is connected with two U-tubes containing calcium chloride; these are connected with a second flask containing 100 c.c. of distilled water, and this to two U-tubes. Each flask with its contents and accompanying U-tubes is weighed; carbon dioxide is then slowly bubbled through for about an hour, and the two sets are re-weighed, and from the weighings the increased solubility of carbon dioxide in the salt solution calculated. Using the dissociation constant of carbonic acid determined by Walker (A., 1900, ii, 268), the authors have determined the dissociation constants of the following acids at 25°: hippuric acid, 2.5×10^{-4} ; nitrous acid, 5.6×10^{-4} ; cacodylic acid, 6.27×10^{-7} ; formic acid, 2.4×10^{-4} ; butyric acid, 1.55×10^{-4} ; propionic acid, 1.33×10^{-5} ; acetic acid, 1.95×10^{-5} ; and benzoic acid, 6.07×10^{-5} . The method obviously makes it possible to determine the dissociation constants of acids which cannot easily be obtained pure, for example, nitrous acid (see also Sand, A., 1904, ii, 612; Bauer, A., 1906, ii, 649).

J. F. S.

Degree of Dissociation of a Dissolved Substance in Saturated Solutions of Different Solvents. PAUL WALDEN (*Bull. Acad. Sci. St. Petersburg*, 1913, 427–448. Compare A., 1906, ii, 527).—The author has determined the solubility of tetramethylammonium iodide in the following solvents at 25°: water, 50% water-ethyl alcohol mixture, methyl alcohol, methyl thiocyanate, acetonitrile, cyanoacetic ester, propionitrile, ethyl alcohol, epichlorohydrin, and acetylacetone. The solubilities in grams per 100 grams of solvent are: 5.268, 3.107, 0.337, 0.229, 0.183, 0.0887, 0.0578, 0.0478, 0.0367, and 0.0275, taking the solvents in the order given above. It is shown that the solubility is parallel with the dielectric constants of the liquids. The electroconductivity of the solutions over a large range of concentration is measured, and the value of λ_{∞} obtained by extrapolation. It is shown that the degree of ionisation of tetramethylammonium iodide in saturated solutions as obtained from $\alpha = \lambda_v / \lambda_{\infty}$ is the same for all the solvents, and has the value $\alpha = 0.666$. The value of α for saturated solutions is compared with the corresponding values for tetraethylammonium iodide and tetrapropylammonium iodide, and it is found that the value decreases with increasing molecular weight, but that the product $\alpha \cdot \Sigma n$, where Σn represents the number of atoms in the molecule, is practically constant, and equal to 12–14. The value of α for saturated solutions is shown in the case of tetrapropylammonium iodide to decrease with increasing temperature; thus, at 0°, $\alpha = 0.305$, whilst at 25°, $\alpha = 0.270$. The paper concludes with a series of orienting experiments on saturated solutions of potassium iodide in water, methyl alcohol, and ethyl alcohol. In this case it is also shown that α is constant and equals 0.423.

J. F. S.

Molten Salts as Solvents. III. The Degree of Dissociation of Dissolved Salts. OTTO SACKUR (*Zeitsch. physikal. Chem.*, 1913, 83, 297—313. Compare A., 1912, ii, 233, 744, 836).—The study of solutions in fused salts is continued in the present paper. It is shown that solutions of silver chloride and cuprous chloride in molten potassium or sodium chlorides lower the freezing point normally up to concentrations of 1 gram-mol. per litre. Further concentration elements of the type $\text{Cu}|\text{CuCl}(\text{dil.})|\text{CuCl}(\text{conc.})|\text{Cu}$ in molten sodium and potassium chloride were measured, and these showed strict adherence to the Nernst hypothesis. All the results showed that these solutions agree with the laws of ideal dilute solutions to within 1% for concentrations up to 1 volume normal. The dissociation of the dissolved substance is independent of the concentration, and is of the order of 10% for the cases investigated (compare Schulze, A., 1913, ii, 193). The difference in the normal potential of silver and copper has the same value in molten potassium chloride solutions at 800° as it has in aqueous solutions at the ordinary temperature. The thermoelectric power of a copper silver couple was measured, and found to be very small; it changes its sign from negative to positive at 675°. J. F. S.

The Dissimulated State in Hydrates. ROBERT DE FORCRAND (*Compt. rend.*, 1913, 156, 1506—1509).—A theoretical discussion of the work of Feytis (compare A., 1911, ii, 1058; this vol., ii, 381), Lebeau (A., 1911, ii, 403), and Chauvenet and Urbain (this vol., ii, 479) on the constitution of hydrates, and in particular of the crystalline hydrates formed by a large number of salts. The author suggests that the stability of these hydrates should be expressed in terms of their heats of solution, referred to one molecule of water. This mode of expression would give a scale varying from 0 to 50 calories, and capable of being determined to 0.1 calorie. W. G.

The Crystallisation of Metals. CECIL H. DESCH (*Proc. Roy. Phil. Soc. Glasgow*, 1911—1912, 43, 107—120).—The structure of crystal skeletons in metals may be examined in three dimensions by the device of photographing serial sections and reconstructing the crystal as a model. The structure of alloys is largely determined by the power of crystalline orientation possessed by their respective components, and the form of a eutectic generally depends on the crystallising power of one component, the other serving as a mere filling material. This is illustrated by the alloys of copper with antimony, and of copper with phosphorus. C. H. D.

Determination of the Size of Colloidal Particles. VICTOR HENRI (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 246—250).—A general résumé of the methods which have been adopted for the determination of the dimensions of colloidal particles. The following methods are noted, and the difficulties and necessary precautions peculiar to each discussed: (1) Direct measurement by means of the ultra-microscope; (2) density determinations of the disperse

system at various heights; (3) measurement of the Brownian movement; (4) measurement of the velocity of settling; (5) diffusion measurements; (6) measurement of the light absorption; and (7) measurement of the intensity of the light dispersed by the particles.

J. F. S.

'The Behaviour of Gels towards Liquids and their Vapours. LUDWIG K. WOLFF and ERNST H. BÜCHNER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1078—1085).—The authors confirm Schroeder's observation (A., 1903, ii, 721) that gelatin, swelling in water vapour, behaves differently from gelatin swelling in liquid water; in the first case, it absorbs much less water than in the second. Agar-agar behaves in a similar manner, as also does celloidin towards ethyl alcohol.

The explanations given by Bancroft (A., 1912, ii, 838) and Freundlich ("Kapillarchemie," p. 494) are discussed; that of Bancroft is considered to be untenable, whilst that of Freundlich is neither very clear nor very convincing; at the same time the authors can offer no better explanation.

T. S. P.

Protein Sols of Continuously Varying Dispersity. WALTER RAMSDEN and N. G. CHAVASSE (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 250—252).—The authors have obtained, by denaturing strong albumin solutions with carbamide, a series of protein colloids which vary from a clear, coagulated protein gel to a series of weak solutions of metaproteins. The differences in the various metaproteins are brought about by suitable changes in the concentration of the carbamide and the albumin. The part played by the carbamide in the denaturing is considered. The authors consider that the main difference between the coagulated protein and the metaproteins consists in a difference in size of the individual aggregates. On comparing a series of sols, the authors note that the greater the concentration of the protein during the denaturing the greater the opalescence, the viscosity, and the influence of acid or alkali on neutral sols with respect to lowering or raising the viscosity. Further, the rate of sedimentation is greater the greater the concentration of the protein during denaturing. From the observations the authors draw the conclusion that the greater the original concentration the greater the size of the individual aggregates, and from the viscosity measurements it is rendered probable that the disperse system consists of small hydrogel protein particles, which, on the addition of acid, shrink, and on the addition of alkali return to their former dimensions, without losing their individuality.

J. F. S.

Precipitation of Colloids by means of Aluminium Hydroxide. JOHN MARSHALL and WILLIAM H. WELKER (*J. Amer. Chem. Soc.*, 1913, 35, 820—822).—Moist aluminium hydroxide, in the form of a thin jelly, has been found capable of completely removing the following substances from their colloidal solutions: copper, gold, platinum, sulphur, nickel sulphide, cobalt sulphide, cupric hydroxide (in sodium hydroxide), Prussian-blue, Congo-red,

azolitmin, litmus (neutral, red, and alkaline), starch (from starch paste and soluble starch), erythrodextrin, starch iodide, fat (from emulsion with water and with soap solution), egg-albumin, globulin (edestin in 5% sodium chloride), gelatin, casein (in half-saturated lime water), glutenin (in 0.5% sodium carbonate), nucleoprotein (in 0.5% sodium carbonate), gliadin (in 70% alcohol), ovomucoid, acid metaprotein (in 0.1% hydrochloric acid), primary proteose, secondary proteose, fat and protein from milk, and protein from blood serum. Oxyhæmoglobin is the only protein tested which was not removed by aluminium hydroxide, and this reagent is therefore well adapted for use in the preparation of oxyhæmoglobin from erythrocytes.

E. G.

The Velocity of Coagulation of Aluminium Hydroxide Sols as Measured by Changes in the Viscosity. HERBERT FREUNDLICH and N. ISHIZAKA (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 230–238).—The rate of coagulation of aluminium hydroxide sols by the addition of electrolytes was followed by viscosity measurements. The results confirm those of Paine (A., 1912, ii, 337) obtained in connexion with copper sols. It is shown that the precipitation time curves exhibit a point of inflexion, and that there is little or no change in the sol immediately the electrolyte is added. The curves obtained from solutions containing different concentrations of the electrolytes are similar, from which it follows that the point of inflexion corresponds with the same value in the increase of the viscosity. Further, it is shown that one curve can be deduced from another by multiplying the time periods of the various degrees of precipitation by the factor for the rate of coagulation. This factor bears a relationship to the concentration of the electrolyte, which is expressed by the equation $V = Lc^p$, where L and p are constants, the value of p varying between 3 and 6. The form of the curves and the high numerical value of p offer a reason for (a) the fact that sols below a given concentration are insensitive to electrolytes, (b) for the frequently observed sudden coagulation. It is further shown that the rate of coagulation of aluminium hydroxide by potassium salicylate can be expressed by the equation $dx/dz = 2kz(1+bx)(1-x)^2$, which, when integrated, gives $k = 1/z^2(1+b)\{b/(1+b) \cdot \log(1+bx)/(1-x) + x/(1-x)\}$, in which x represents the fraction precipitated, z the time, b and k constants, b being independent of the concentration of the electrolyte, and a function of the x value for the point of inflexion, and k being a function of the concentration of the added electrolyte. The rate of coagulation constant k is related to the concentration of the electrolyte as indicated by the equation $k = \lambda c^q$. The maximum viscosity of an aluminium hydroxide sol, which is completely precipitated by the addition of an electrolyte, increases with the quantity of colloid in the sol. The maximum viscosity is dependent in a degree on the nature of the precipitating electrolyte. The viscosity is smaller with NO_3 and CNS anions than with sulphion and succinate ion. The maximal viscosity varies in concentrated sols on shaking.

J. F. S.

Chemical Time Reactions with Colloids. DANIEL VORLÄNDER and REINHOLD HABERLE [with WALTER STRUBE] (*Ber.*, 1913, 46, 1612—1628).—The authors have investigated the time reactions between colloidal solutions of Prussian-blue and arsenious sulphide respectively and alkalis. When sodium hydroxide is added to a dialysed solution of Prussian-blue, the colour does not disappear instantaneously but fades gradually; the rate of reaction increases with rise in temperature and with increase in concentration of the sodium hydroxide. The rate of reaction is, however, not proportional to the concentration of the hydroxide ions; it is quickest with barium hydroxide, and slowest with sodium and potassium hydroxides, strontium and calcium hydroxides falling in between. Tetramethylammonium hydroxide has a slower action than alkali hydroxide. The velocity does not depend on the solubilities of the respective ferrocyanides formed. Similar results hold when arsenious sulphide is used instead of Prussian-blue.

The observed time reactions thus depend on the nature of the cation and also on the concentration of the hydroxide ion. Before the actual chemical reaction occurs, adsorption of the hydroxides or of their ions takes place, and this adsorption may be the most rapid in the case of barium hydroxide.

It would be assumed that neutral salts would increase the particles of the hydrosol by adsorption and also surround them, and thus retard the action of alkalis; this is not the case, however, since sodium chloride greatly accelerates the action of sodium hydroxide. If the sodium chloride is added to the solution of, for example, Prussian-blue, before the sodium hydroxide, the acceleration is not so great as when it is added after the sodium hydroxide.

The action of neutral salts is very varied, not always being one of acceleration. A large number of examples are given, showing that the action is an individual one, depending on the salt.

The reaction also depends on the relative concentrations of the colloid, alkali, and neutral salt; for example, by varying the concentration of the Prussian-blue solution, a concentration can be found where the addition of barium chloride has no effect on the rate of reaction with barium hydroxide. Above this concentration the barium chloride has an accelerating, and below it a retarding, action. Also, Prussian-blue is decomposed more slowly by a large than by a small quantity of calcium hydroxide solution.

Contrary to the usual statement (compare Linder and Picton, *T.*, 1892, 61, 127; Billiter, *A.*, 1905, ii, 305), the authors find that arsenious sulphide does not hydrolyse when suspended in water. They also find that very dilute solutions of arsenious acid and hydrogen sulphide can be mixed without giving a yellow solution of arsenious sulphide. If this solution contains a compound, it is very unstable, being partly hydrolysed into arsenious acid and hydrogen sulphide.

Arsenious acid gives no time reaction with alkalis. Time reactions in the formation of salts from bases and acids, including acid anhydrides and thio-acid anhydrides, are only known with

typical colloids, such as silicic acid, and the sulphides of arsenic, antimony, and tin. Carbon dioxide must also be included.

T. S. P.

The Kinetics of Ammonium Salts. EDGAR WEDEKIND (*Zeitsch. physikal. Chem.*, 1913, 83, 370—372).—Polemical against Halban (see A., 1908, i, 723; 1909, ii, 722; 1911, i, 852; this vol., i, 354, 355).

J. F. S.

The Kinetics of Ammonium Salts. HANS VON HALBAN (*Zeitsch. physikal. Chem.*, 1913, 83, 373).—Polemical. An answer to Wedekind and Paschke (see preceding abstract).

J. F. S.

Polymorphism. III. Equilibria in Binary Systems with a Polymorphic Substance. EFISIO MAMELI and ANNA MANNESSIER (*Chem. Zentr.*, 1913, i, 1665; from *Boll. Soc. Med. Chirur. Pavia*, 1912, pp. 17. Compare this vol., ii, 19).—The melting-point curves of mixtures of the α - and β -forms of chloroacetic acid with naphthalene, piperonal, and acetic acid have been studied. The two modifications behave in the same way. While they act as dissolved substances, the curves fall together, and in the converse case the curves are parallel. Naphthalene shows two eutectic points, but the other substances give irregularities in the neighbourhood of the eutectic point, due to supersaturation and partial crystallisation.

J. C. W.

Equilibria in Ternary Systems. IV. and V. FRANS A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1200—1213, 1213—1228).—Further theoretical discussion of the conditions of a liquid saturated with a solid and in equilibrium with the vapour.

T. S. P.

Equilibria in Quaternary Systems. VII. Lines of Solidification of Quaternary Mixtures from which Binary or Tertiary Mixed Crystals Separate. NICOLA PARRAVANO (*Gazzetta*, 1913, 43, i, 454—469. Compare this vol., ii, 33, 140).—From a homogeneous, quaternary liquid, the following may separate on cooling: (1) the pure components; (2) binary mixed crystals; (3) ternary mixed crystals; (4) quaternary mixed crystals. Having already dealt with the first and last of these cases, in the present paper the author gives a mathematical analysis of the problems presented by the second and third in the case where there is complete miscibility both in the solid and in the liquid state.

R. V. S.

Equilibria in Quaternary Systems. VIII. Quaternary Systems with Binary Mixed Crystals with a Gap of Miscibility. NICOLA PARRAVANO (*Gazzetta*, 1913, 43, i, 469—488. Compare preceding abstract).—In the present paper the author gives a mathematical discussion of two of the chief types of the systems

mentioned, namely, those with a binary diagram of Roozeboom's type V, and those with a binary diagram of Roozeboom's type IV.

R. V. S.

Velocities of Reaction and Equilibria. FRANS E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1109—1117).—The author extends the theory put forward by himself and Kohnstamm (*ibid.*, 1911, 789) with respect to the relation between the velocity of reaction and the thermodynamic potentials of the substances participating in the reaction (compare also A., 1912, ii, 328), and shows that the relation between the velocity constant and the temperature is given by the equations: $d \log k / dt = (\epsilon_i - \epsilon) RT^2$ and $\log k = (\epsilon - \epsilon_i) / RT - B$, where ϵ_i and ϵ represent the values of the energy of the intermediate transitional stage of the reaction and of the initial system respectively. The greater part of the known experimental data allows the substitution of a constant value for $\epsilon - \epsilon_i$.

T. S. P.

Limited Displacement of Monoethylamine by Ammonia Gas. FÉLIX BIDEZ (*Compt. rend.*, 1913, 156, 1613—1615. Compare A., 1905, i, 686; 1912, ii, 915; this vol., ii, 197).—A study of the systems ammonia-ethylamine hydrochloride and ethylamine-ammonium chloride, the equilibrium pressures being measured at various temperatures. In both systems the equilibrium pressures rise with increase in temperature; the values in the two cases whilst in agreement at low temperatures differ considerably from 15° to 23·2°. In no case was any free ethylamine obtained at the end of the reaction. The system ammonia-ethylamine hydrochloride is similar in behaviour to the systems ammonia-amyamine hydrochloride and ammonia-ethylenediamine hydrochloride (*loc. cit.*), and fits in with the theory proposed admitting the existence of several basic salts formed by the action of the amine, displaced by the ammonia, on the initial neutral hydrochloride or on a basic hydrochloride already formed.

W. G.

Laws of "Concentrated" Solutions. V. Part I. Equilibrium between Arsenious Acid and Iodine in Aqueous Solution. Part II. General Law for Chemical Equilibrium in Solutions containing Ions. Part III. Energetics of the Reaction between Arsenious Acid and Iodine. EDWARD W. WASHBURN and EARLE K. STRACHAN (*J. Amer. Chem. Soc.*, 1913, 35, 681—714).—The reaction between arsenious acid and iodine has been studied by Roebuck (A., 1903, ii, 14; 1906, ii, 76), but the value of the equilibrium constant calculated from his data is very uncertain owing to certain sources of error in his work. The reaction has now been re-investigated.

Determinations of the distribution ratio of iodine between carbon tetrachloride and water have given the value 85·0. Measurements of the equivalent conductivity of hydriodic acid solutions at 25° have furnished the following results, which are more than 2% higher than the values obtained by Ostwald: 0·15*N*, 389·5; 0·1*N*,

395.6; 0.08*N*, 398.5; 0.05*N*, 404.3. A study of the iodide-tri-iodide equilibrium in solution of hydriodic acid has been made by shaking solutions of iodine in hydriodic acid with carbon tetrachloride at 25° until equilibrium was established, and has yielded for the constant $[I_2][I^-]/[I_3^-]$ a value of $(1.30 \pm 0.015)10^{-3}$ for total ion concentrations between 0.05 and 0.15 equivalents per litre. In a mixture of HI and HI_3 , both acids are ionised to the same extent. The value of Λ_0 for the $H_2AsO_4^-$ ion at 25° is 36 reciprocal ohms. The ionisation of arsenic acid at 25° is given by the relation $[H^+][H_2AsO_4^-]/[H_3AsO_4] = 10^{-3}(4.32 + 4C_i)$, where C_i is the total ion concentration of the solution. The basic ionisation constant of arsenious acid at 25° is $[AsO^+][OH^-]/[H_3AsO_3] = 0.15 \times 10^{-14}$, in a solution with an ion concentration of 0.1 equivalent per litre. The value of the equilibrium expression

$$[H_3AsO_4][H^+]^2[I^-]^3/[H_3AsO_3][I^-]^3 = K_c$$

was determined by bringing a standard aqueous solution of arsenious acid in contact with a solution of iodine in carbon tetrachloride, and was found to be 5.5×10^{-2} .

The results show that the equilibrium $H_3AsO_3 + I_3^- + H_2O = H_3AsO_4 + 2H^+ + 3I^-$ obeys the law of mass action within the experimental error over a fairly wide range of concentrations. This is in marked contrast to the great deviation from the requirements of the law of mass action shown by the ionisation of a strong electrolyte. This behaviour is discussed from a thermodynamic point of view, and a general law is deduced for chemical equilibrium in solutions containing ions. On calculating K_c for the equilibrium between arsenious acid and iodine on the basis of this law, a result is obtained agreeing closely with the results of the experiments.

The heat of the reaction between arsenious acid and iodine is 1360 cal. The general expression for K_c is $\log_{10} K_c = -1.3495 + 0.00372i$. The free energy of the reaction is $-\Delta F^\circ = RT \log_e K_c = 5690 + 5.42T$ joules, in an aqueous solution having a constant ion concentration of 0.1 equivalent per litre. The potential of the normal arsenic electrode has been calculated, on the assumption that the potential of the normal iodine electrode is 0.256 volt when measured against the calomel electrode, and has been found to be 0.293 volt.

E. G.

Stratified Disperse Systems. RAPHAEL ED. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 269—273).—The author considers theoretically the reasons for the formation of layers in the structure of certain naturally occurring mineral deposits and of certain organic deposits. The theory advanced is that, given a solution which is very slowly evaporating in the absence of crystal centres, a supersaturation will take place and the solution become increasingly concentrated until the limit of the metastable region is reached; then there will be a deposit. If now the crystal centres are removed in some way, a further period of supersaturation will occur, and consequently later a second layer. It is possible this may be brought about by the supersaturation of a

second constituent of the solution crystallising over the first layer or by the adsorption of a colloidal substance, such as silica, which is known to greatly hinder further deposition of the same crystal sort. This theory is discussed in connexion with the layer formation of gallstones, urinary calculi, oolite formation, agate formation, layer crystals, and the layers of anhydrite in the Stassfurt deposits.

J. F. S.

The Combustion of Gaseous Mixtures and the Retardation of Ignition. J. TAPPANEL and LE FLOCH (*Compt. rend.*, 1913, 156, 1544—1546).—A study of the retardation of ignition of mixtures of methane and air at various temperatures, the time of ignition being obtained by measuring the variations in pressure. Near to the ignition temperature the retardation is very marked, and reaches in some cases ten seconds. The intervals before ignition are much shorter with higher pressures. The retarding effect is just as marked when water vapour is introduced into the explosive mixture, the retardation not being due therefore to the gases being dry. A slow reaction goes on during the time before actual ignition occurs.

W. G.

Study of the Velocity of Reaction between Phenol and Formaldehyde. BENJAMIN JABLONOWER (*J. Amer. Chem. Soc.*, 1913, 35, 811—820).—Although the reaction between phenols and formaldehyde has been made the subject of many investigations, it does not seem to have been studied from a physico-chemical standpoint.

It has been observed that when phenol is heated with formaldehyde solution in presence of a little ammonia as condensing agent, the liquid gradually increases in viscosity, and this suggested that the reaction might be studied by viscosity measurements. This was found impracticable, however, and an attempt was therefore made to investigate the velocity of the reaction by observing the density at regular intervals. The results indicate that under certain conditions the density increases regularly with the time of heating, but that in other cases the rate of increase in density decreases with the time of heating. The rate of increase of density rises with the temperature and with the quantity of ammonia present. The most regular results were obtained when the largest excess of formaldehyde was used. An equation is suggested for calculating the increase of density.

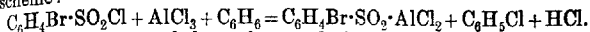
These results were obtained by comparatively crude experiments, and must not be regarded as strictly accurate.

E. G.

The Velocity of Substitutions in the Benzene Nucleus. FRANS E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1118—1128).—The theory given in the previous paper (this vol., ii, 572) is tested by application to the data obtained by Holleman and his co-workers on nitration and bromination of various aromatic compounds, and found to give satisfactory results. The conclusion is come to that the substitution entropies are identical for different positions in the nucleus.

T. S. P.

Dynamic Researches Concerning the Reaction of Friedel and Crafts. SIMON C. J. OLIVIER and JAKOB BÖESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1069—1077).—The authors have measured the velocity of the action of *p*-bromobenzene-sulphonyl chloride on an excess of benzene in the presence of aluminium chloride, the acid chloride being selected, since it is not decomposed by cold water, whereas it is rapidly decomposed on warming with aqueous silver nitrate, so that the unattacked sulphonyl chloride could be freed by means of cold water from aluminium chloride, and the hydrochloric acid formed and subsequently titrated with standard silver nitrate solution. Attempts to carry out experiments in carbon disulphide solution were unsuccessful, since reaction then proceeded in accordance with the scheme:



The authors are led to the conclusion that the reaction takes place in two phases:

- (i) $\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2\text{Cl}\cdot\text{AlCl}_3 + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2\text{Cl}\cdot\text{AlCl}_3\cdot\text{C}_6\text{H}_6$,
 - (ii) $\text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2\text{Cl}\cdot\text{AlCl}_3 + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_4\text{Br}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5\cdot\text{AlCl}_3 + \text{HCl}$,
- of which the first represents the real catalytic action resulting in the formation of a ternary compound, which proceeds slowly in regard to (ii). They consider, further, that the catalytic action of aluminium chloride is not attributable to its ability to combine with one of the molecules, since the free aluminium chloride is much more active than the combined portion, but is based on an influence, termed dislocation, which makes itself felt before the real compound has been formed. In harmony therewith it appeared that there was measured an additive action of the acid chloride with benzene, the first rendered active only so far as it is united with aluminium chloride, the second rendered active by the total aluminium chloride present.

Similar experiments have been made with toluene, chlorobenzene, bromobenzene, and nitrobenzene. H. W.

The Preservation of Hydrogen Peroxide. JAMES H. WALTON, jun., and ROY C. JUDD (*Zeitsch. physikal. Chem.*, 1913, 83, 315—335).—The paper deals with the velocity of decomposition of 30% hydrogen peroxide at 80°. It is shown that the gasometric method of determining the rate of decomposition of hydrogen peroxide at this temperature leads to results which are inconcordant and not reproducible. It is surmised that the shaking of the solution introduces a factor into the decomposition of hydrogen peroxide which cannot be taken into reckoning. It is shown that the nature of the vessel in which the hydrogen peroxide is placed has a decided influence on the rate of decomposition, not on account of the nature of the surface of the glass, but rather on account of something dissolved out of the glass. Jena flasks which have been boiled with concentrated hydrochloric acid and then steamed for weeks give a minimum rate of decomposition. Such flasks allow of the determination of the velocity constant for a unimolecular reaction being obtained, and the same results can be

obtained when different flasks are employed. The rate of decomposition is much smaller in quartz flasks than in Jena glass flasks. Conductivity water which has been preserved in the steamed Jena glass flasks dissolves sufficient from the glass in a few hours to bring about an increased velocity of decomposition of hydrogen peroxide. Solutions of sodium silicate, sodium carbonate, and sodium hydroxide act catalytically on hydrogen peroxide, whereas calcium hydroxide does not affect the rate of decomposition. A solution of powdered glass decomposes hydrogen peroxide very readily; this is probably due to the presence of a metallic oxide dissolved out of the glass. Acetanilide acts towards hydrogen peroxide as a negative catalyst; it preserves hydrogen peroxide solutions even when they contain positive catalysts if it is present to the extent of 0.00148 mol. per litre, and in this respect it is superior to sulphuric acid. Concentrated solutions of sodium chloride preserve hydrogen peroxide, but when a positive catalyst, such as sodium hydroxide, is present, it has little action. Sulphuric acid is the most effective preservative for hydrogen peroxide; even when it is present to the extent of only 0.00066 gram per litre, it retards the decomposition in a marked degree. It retards the reaction more the more concentrated it is, but there is apparently no simple relationship between the amount of retardation and the concentration of the acid. J. F. S.

The Sensitiveness of Some Chemical Reactions. MARJAN GÓRSKI (*Zeitsch. anorg. Chem.*, 1913, 81, 315—346. Compare Böttger, A., 1910, ii, 195).—The atomic sensitiveness is defined as the largest volume in litres in which at least one gram-atom or gram-molecule must be dissolved, in order that the reaction may be just visible. A beam of light from an arc is used as a means of detecting turbidity, and water repeatedly filtered through toughened paper is used.

The sensitiveness is found to increase with the concentration of the reagent used, and the precipitate in certain cases, such as that of barium sulphate, becomes more visible with time. The sensitiveness in this reaction is greater with an excess of potassium sulphate than with an excess of barium chloride, and similar conditions occur with calcium oxalate. Mercurous chloride is also obtained as a crystalline precipitate, whilst silver bromide and iodide are colloidal. As a colour reaction, that between cobalt salts, potassium thiocyanate, and alcohol has been studied. A comparison is made between this method of testing and the micro-chemical and spectroscopic methods, and the sensitiveness of a large number of qualitative reactions is tabulated. C. H. D.

Catalysis. XV. Reactions of Both the Ions and the Non-ionised Forms of Electrolytes. SOLOMON F. ACREE (*Amer. Chem. J.*, 1913, 49, 345—368).—Evidence in favour of the view that both ions and non-ionised molecules may be concerned in all chemical reactions is adduced from a re-interpretation of the work of Arrhenius, Ostwald, Bredig, Goldschmidt, Stieglitz, and others,

as well as from the researches of the author and his co-workers. The latter investigations were made with concentrations varying from N to $N/64$, but experiments have now been undertaken to study the reversible addition of ethyl alcohol to p -bromobenzonitrile, and the catalytic effect of sodium, potassium, and lithium ethoxides in solutions as dilute as $N/2048$. The results so far obtained support the theory that both ions and non-ionised electrolytes are active in both concentrated and "ideal" solutions.

E. G.

Catalysis. XVI. Reactions of Both the Ions and the Non-ionised Forms of Electrolytes. Reversible Addition of Alcohols to Nitriles Catalysed by Sodium Ethoxide. ELI K. MARSHALL, jun., JULIA PEACHY HARRISON, and SOLOMON F. ACREE (*Amer. Chem. J.*, 1913, **49**, 369—405).—In an earlier paper (Marshall and Acree, this vol., i, 253), an account was given of a study of the addition of alcohols to nitriles in presence of ethoxides as catalysts. A further investigation of these reactions has been made as well as of the reversible change of ethyl iminoacetate and iminobenzoate into the corresponding nitrile and ethyl alcohol.

The results prove that the action of sodium ethoxide in these reactions is purely catalytic, and that the velocity of the non-catalysed reaction is so small as to be negligible. A comparison of the reaction-velocities and the conductivity data shows that the ethoxide ions have a definite effect on the velocity which can be expressed as a simple function of their concentration. The non-ionised sodium ethoxide also has an influence which can be expressed as a simple function of the concentration of the molecules. On referring all data to the N -solution and using K_i and K_m to express the effect of a gram-equivalent of the ethoxide ions and of the non-ionised sodium ethoxide respectively, constant values are obtained for K_i and K_m whatever the concentration of the ethoxide. For benzonitrile and ethyl iminobenzoate, $K_i:K_m=0.1172:0.0976$, and for acetonitrile and ethyl iminoacetate $K_i:K_m=0.344:0.228$.

The addition of sodium iodide in these reactions produces a "salt effect," which is due chiefly to a change in the concentrations of the ions and molecules as required by the theory of isohydric solutions.

The catalytic action of sodium ethoxide on the decomposition of imino-esters is analogous to the reactions of alkyl haloids with ethoxides and phenoxides and with sodium 1-phenyl-3-thiourazole. In all these cases, the velocity of the reaction can be expressed as a function of the concentration of the ions increased by a function of the concentration of the non-ionised molecules.

E. G.

Representation of the Chemical Elements by means of Points in Ordinary Space. ARNALDO PIUTTI (*Atti R. Acad. Lincei*, 1913, [v], **22**, i, 569—575).—The author describes a representation of the elements in three dimensions. He follows Borchers and Schmidt (compare Schmidt, A., 1911, ii, 198) in plotting on two rectangular co-ordinates atomic weights and equivalent volumes,

and in regarding the ordinates as positive or negative according as the elements are electropositive or electronegative, but he adds on a third axis the specific heats of the elements, chosen as far as possible between 0° and 100° . In view of the law of Dulong and Petit, the projection of the elements on the plane of the axes of atomic weights and specific heats satisfies the equation $xz=6.4$, that is, it is an equilateral hyperbola the asymptotes of which are the axes of x and z . Hence the points representing the elements lie on an equilateral hyperbolic cylinder. Further, since atomic weights and specific heats are essentially positive, all the points lie on one fold of the cylinder. The elements with atomic weights less than 6.4 lie on one side of the straight line forming the locus of the vertex of the hyperbola of the sections parallel to the plane xz , those with atomic weights greater than this (that is, all the elements except hydrogen and some extraterrestrial elements) on the other side. A plane representation of the space diagram is also given.

R. V. S.

The Present Position of Mendelée's Periodic System of the Elements. MAURICE CRAEBÉ (*Bull. Soc. chim. Belg.*, 1913, 27, 153—159).—A review especially of some of the more recent investigations on the relation between the atomic weights of the elements.

D. F. T.

Some Consequences of Graham's Work: the Nature of Elements; the Diffusion of Liquids. HENRY E. ARMSTRONG (*Proc. Roy. Phil. Soc. Glasgow*, 1911—12, 43, 67—96).—The Graham Lecture. A discussion of the periodic system; the chemical nature of the inactive gases; the process of diffusion; and the nature of hormones.

C. H. D.

[The Nature of Auxiliary Valencies.] FRITZ EPHEHAIM (*Zeitsch. physikal. Chem.*, 1913, 93, 257—259).—Polemical. An answer to Friedrichs (this vol., ii, 497; see also this vol., ii, 129, 130; A., 1912, ii, 546).

J. F. S.

Magnesia Apparatus. EDGAR WEDEKIND (*Zeitsch. angew. Chem.*, 1913, 26, 303—304).—An extension of the applications of apparatus made of magnesia, or rather a mixture of magnesia and kaolin (compare A., 1912, ii, 382). The articles mentioned are spatulas, for flame tests; shallow troughs for containing sodium chloride, which, when heated in a Meker burner, give a constant source of sodium light; crucibles, and boats; test tubes. The articles will stand a temperature of 1300° . Tubes cannot be made to stand a vacuum, or for use with pure gases, since the material is porous.

T. S. P.

A New Apparatus for Collecting Sediments from Turbid Liquids and for Extracting Liquids. EDUARD SPAETH (*Zeitsch. angew. Chem.*, 1913, 26, 304).—The apparatus is an improvement on the author's sedimentation glass (A., 1897, ii, 281). It consists

essentially of an extraction funnel fitted with a special stop-cock. A small cavity is made in one part of the stop-cock; when put in connexion with the funnel it collects any sediment. The stop-cock is also bored in such a way that liquid contained in the funnel can be run out through the main body of the cock itself.

The funnel possesses a flat side, so that it will not roll about when laid down; it can also be placed on a water-bath and heated.

T. S. P.

Inorganic Chemistry.

Production of Hydrogen from Water and Coal from Cellulose at High Temperatures and Pressures. FRIEDRICH BERGIUS (*J. Soc. Chem. Ind.*, 1913, 32, 462—467).—According to Noyes, the dissociation of water increases nearly 2000-fold between the boiling and critical points. It should therefore be a fairly strong acid at high temperatures, if kept in the liquid condition, and in accordance with this the author has been able to obtain hydrogen in quantity by heating water and iron under pressure (not stated) at about 300°. The action is accelerated by the presence of ferrous chloride and copper. Ferroso-ferric oxide is the product of reaction.

In the decomposition of cellulose by heat, the reaction is strongly exothermic, and under ordinary experimental conditions it is impossible to maintain the temperature constant. This can be done, however, by making use of the high specific heat of water; the cellulose is heated with water under high pressures. At 340°, after about twelve hours, pure cellulose yields a black powder, which proves to be soft coal of about 84% C, 5% H, and 11% O, the reaction being probably: $4C_6H_{10}O_5 = C_{24}H_{16}O_2 + 3CO_2 + 12H_2O + 70,000 \text{ cal.}$ The percentage of carbon rises with the length of heating and the temperature at which the reaction takes place, reaching a final value of 84% C. Peat gives similar results to cellulose. The reaction takes place much more quickly at 340° than at 310°, the temperature quotient being approximately 2.

The coal produced has the composition and all the qualitative reactions demanded by Donath for fossil coal, but it differs very much in its physical properties, as it is a very finely divided black powder. It may be converted into a substance with all the physical properties of natural coal by heating it above 300° under very high pressure (5000 atmospheres).

The author's experiments lead him to the conclusion that the formation of coal in nature takes place in two distinct reactions, namely, first the reaction of carbonisation, and secondly, the formation of anthracite under pressure. Without pressure, no formation of anthracite can occur.

T. S. P.

Expulsion of Acids by Hydrogen Peroxide. JOACHIM SPERBER (*Chem. Zentr.*, 1913, i, 1490—1491; from *Schweiz. Nocht. Chem. Pharm.*, 1913, 51, 166—169).—A description in the terms of the theoretical views expressed in a former paper (this vol., ii, 400) of the action of hydrogen peroxide on some salts. The liberated hydroferrocyanic acid, in the case of its potassium salt, is frequently oxidised to Prussian-blue, which is then decomposed by the free alkali. J. C. W.

Optical Investigation of Solidified Gases. III. The Crystalline Properties of Chlorine and Bromine. WALTER WAHL (*Proc. Roy. Soc.*, 1913, A, 88, 348—353).—Chlorine crystallises in the orthorhombic system, the crystals in sections both parallel and at right angles to the principal axis being strongly double-refracting; also the extinction between crossed nicols is parallel to the principal axis, as indicated by the cleavage. No polymorphic change was observed at temperatures between that of the melting point and that of liquid air. As the temperature falls to that of liquid air, the pale yellow colour of the crystals gradually decreases in intensity, until scarcely any colour is left. The crystals are slightly pleochroic.

Crystallised bromine is very similar to crystallised chlorine, except that all the properties appear more pronounced. The crystals, which belong to the orthorhombic system, are strongly pleochroic; the absorption is dark brownish-red in the direction of the prism axis, yellowish-red in the direction of a line bisecting the smaller prism angle, and pale yellowish-green in the direction of the line bisecting the larger prism angle. With decreasing temperature the intensity of the colour of the crystals gradually diminishes, becoming very pale yellow at the temperature of liquid air; this is due to the gradual disappearance of the strong trichroism.

A comparison of the crystalline properties of chlorine, bromine, and iodine is given. Pleochroism occurs with each element, its strength and character changing and increasing as the atomic weight increases. The three elements may be regarded as perfectly isomorphous. T. S. P.

The Dynamic Allotropy of Sulphur. HUGO R. KRUYT (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1228—1236).—Mainly a criticism of Leeuw's paper on the relation between the modifications of sulphur (this vol., ii, 40), fresh experiments having been carried out in support of the criticism. The experiments show that the change in volume of strongly supercooled sulphur over the temperature range 70—95° is different from that observed by Leeuw, and that the phenomena occurring have no connexion with the change $S_{rh} \rightleftharpoons S_{mon}$. The author maintains the conclusions drawn from his previous work (compare this vol., ii, 132). T. S. P.

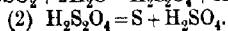
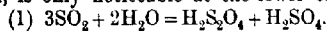
A New Modification of Sulphur. II. ADRIAAN H. W. ATEN (*Zeitsch. physikal. Chem.*, 1913, 83, 442—458. Compare this vol., ii, 40).—A continuation of the work published in the previous

paper. The author shows that sulphur which has been heated to 170° and rapidly cooled contains just as much S_8 as sulphur which has been heated to 445° and then rapidly cooled. It is shown that in sulphur chloride solution S_8 changes fairly rapidly into S_6 . Experiments were then made in toluene solution, and it was shown that the solubility of sulphur which has been heated at 170° is greater than sulphur which has not been treated in this way; also it is shown that the solubility in the case of the treated sulphur is greater the larger the quantity of solid sulphur present. The increased solubility is studied in the light of a number of hypotheses, and it is shown that S_6 must be present in the solid sulphur either as mixed crystals with S_8 or as a mixture; the experiments do not allow of an answer as to which form it is present. The solutions containing S_6 are all strongly coloured yellow; this colour is shown to be due to sulphur and not to an impurity; in the case of a solution in carbon disulphide containing 18 atoms %, the colour was that of a strong aqueous solution of potassium chromate. On cooling a solution of $S_6 + S_8$ to -80° , the whole of the S_6 separated out, leaving only S_8 in solution.

Experiments were made to obtain solid S_6 by evaporating the solvent, but in the first experiments a white, amorphous powder, insoluble in carbon disulphide and toluene, was obtained, namely, S_8 . If the solvent was removed at -80° by reduction of pressure, the residual sulphur was practically all soluble in toluene, with a small residue of S_8 ; so that on distillation of a solution of S_6 the dissolved substance is transformed into S_8 . It is shown to be extremely unlikely that the solutions of S_6 are really solutions of S_6 . Two solutions of S_6 and $S_6 + S_8$ were submitted to a strong light; this caused an immediate precipitation of S_8 , less, however, in the case of $S_6 + S_8$ than in the other case, whereas if S_6 is really S_6 , the greater precipitation should have come from the $S_6 + S_8$.

J. F. S.

Reactions Between Water and Sulphurous Acid at Different Temperatures. Formation of Hyposulphurous Acid. ÉMILE JUNGLEISCH and LÉON BRUNEL (*Compt. rend.*, 1913, 156, 1719—1724).—A study of the effect of heating aqueous solutions of sulphur dioxide, saturated at 0° , at different temperatures from 160° downwards. Water and sulphur dioxide will react at temperatures below 160° , and even at the ordinary temperature producing sulphur and sulphuric acid, but the reaction is much slower at the lower temperatures and with more dilute solutions. This production of sulphur and sulphuric acid really takes place in two stages, the first of which, resulting in the formation of hyposulphurous acid, is only noticeable at the lower temperatures:



Certain secondary reactions of a minor character take place at the same time.

W. G.

Study of the Metallic Tellurites. VICTOR LENHER and EDWARD WOLESENSKY (*J. Amer. Chem. Soc.*, 1913, **35**, 718—733).—A study has been made of various metallic tellurites. In the case of the alkali metals, mono-, di-, and tetra-tellurites have been prepared, the first two by fusing tellurium dioxide with calculated quantities of the alkali carbonates, and the tetratellurites by decomposing the ditellurites with water. The tellurites of the other metals have been obtained by precipitation from a solution of a salt (usually the chloride) with sodium tellurite. The alkali tellurites are soluble in water, the alkali-earth salts slightly soluble, and those of the heavy metals are insoluble. Tellurites are unstable; at the ordinary temperature and in presence of moisture, tellurous acid is readily displaced by carbon dioxide. When heated in the air at 440—470°, the tellurites undergo oxidation, but neither the tetratellurites nor tellurium dioxide are oxidised under these conditions. In the case of potassium ditellurite, the oxidation results in the formation of the compound, K_2O, TeO_3, TeO_2 . The precipitated tellurites are flocculent and amorphous, and, with the exception of the magnesium salt, do not show any tendency to crystallise.

The following salts have been prepared: Potassium tellurite, $K_2TeO_3, 3H_2O$, ditellurite, and tetratellurite, $K_2Te_4O_9, 4H_2O$; sodium tellurite, $Na_2TeO_3, 5H_2O$, ditellurite, and tetratellurite, $Na_2Te_4O_9, 4H_2O$. Ammonium tellurite probably exists in solution and also in the solid state when surrounded by a saturated solution of tellurous acid in ammonia, but on attempting to isolate it, it decomposes spontaneously at the ordinary temperature with formation of hydrated tellurium dioxide. Magnesium tellurite forms at least two definite hydrates, $5MgTeO_3, 9H_2O$ and $10MgTeO_3, 9H_2O$. Barium tellurite, precipitated from barium chloride solution, occludes large quantities of the chloride which cannot be completely removed by washing. Silver tellurite is anhydrous; it can be obtained in several varieties, differing from one another in colour. Manganous tellurite is very unstable, and is oxidised by the air at the ordinary temperature, the metal being converted into the tervalent state. Cadmium tellurite, $3CdTeO_3, 2H_2O$; nickel tellurite, $NiTeO_3, 2H_2O$; cobalt tellurite, $CoTeO_3, H_2O$; and lead tellurite, $3PbTeO_3, 2H_2O$, are also described.
E. G.

Some Reactions of Hydrazine Nitrate. WILLIAM R. E. HODGKINSON (*J. Soc. Chem. Ind.*, 1913, **32**, 519—520).—Hydrazine nitrate, N_2H_4, HNO_3 , has m. p. 70°, and may be kept at 100° for a long time without change. At 200° in a vacuum it decomposes in accordance with the scheme: $4N_2H_4, HNO_3 = 5N_2 + 2NO + 10H_2O$. When heated under pressure, it explodes violently; at ordinary pressures it burns rapidly. The aqueous solution has very little action on metals such as zinc, cadmium, and magnesium, which are strongly acted on by a solution of ammonium nitrate, but the fused salt acts more vigorously than fused ammonium nitrate. Zinc, copper, and most other metals, as well as oxides, sulphides,

nitrides, and carbides, cause a flaming decomposition at temperatures little above the melting point. Cobalt and nickel that have been thoroughly melted behaved like the other metals towards fused hydrazine nitrate, but commercial cube cobalt causes a very violent action, followed almost immediately by a severe explosion.

Nitrates of bases, such as aniline and toluidine, both in solution and when fused, behave towards most of the metals in a way analogous to ammonium nitrate.

T. S. P.

Behaviour of the Hydronitrogens (Nitrogen Hydrides) and their Derivatives in Liquid Ammonia. IV. Pressure Concentration Isotherms in the System Ammonia, Ammonium Trinitride [Azoimide]. ARTHUR W. BROWNE and A. E. HOULEHAN (*J. Amer. Chem. Soc.*, 1913, 35, 649—658. Compare Browne and Welsh, A., 1911, ii, 1084; Browne and Houlehan, A., 1911, ii, 1085).—An account is given of experiments on the two-component system, ammonia, ammonium azoimide, in which pressure-concentration isotherms were studied at 20°, 0°, and -33°. The results show that ammonium azoimide unites with ammonia to form a diammonate, $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$, which crystallises in colourless, transparent, elongated plates. This compound is stable at -33°, showing a dissociation pressure of about 22·8 cm. at this temperature, but is not stable at 0°; the inversion point is about -9°. One gram of liquid ammonia dissolves 0·7 gram of ammonium azoimide at -33°, and 1 gram at 0°. The vapour pressures of solutions saturated at these temperatures are 43·7 and 149 cm. respectively.

E. G.

Behaviour of the Hydronitrogens (Nitrogen Hydrides) and their Derivatives in Liquid Ammonia. V. Electrolysis of a Solution of Ammonium Azoimide in Liquid Ammonia. ARTHUR W. BROWNE and M. E. HOLMES (*J. Amer. Chem. Soc.*, 1913, 35, 672—681).—Browne and Houlehan (A., 1911, ii, 1085) have shown that when a solution of ammonium azoimide in liquid ammonia is treated with certain metals, the following reaction takes place: $\text{M} + \text{NH}_4\text{N}_3 = \text{MN}_3 + \text{NH}_3 + \text{H}$. It follows therefore that the solution is virtually a solution of free azoimide, and, as such, affords a convenient means of studying the properties of this substance in an anhydrous condition.

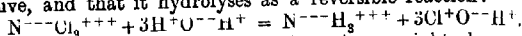
In the present paper an account is given of the behaviour of a solution of ammonium azoimide in liquid ammonia towards the electric current, the experiments being undertaken with a view to gaining information on the properties of the discharged N_3' ion.

It has been found that such solutions readily conduct the electric current, and that, when platinum electrodes are used, electrolysis takes place with liberation of hydrogen at the cathode and nitrogen at the anode. The ratio $\text{H}_2 : \text{N}_2$ varies from 1·65 to 2·15, with an average of 1·93, instead of the ratio 0·333, which would result if the discharged N_3' ions simply broke up into molecular nitrogen. These facts are best explained on the assumption that some of the discharged N_3' ions break up into molecular nitrogen, but that

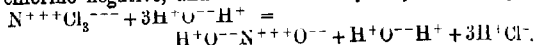
most of them react with ammonia to regenerate ammonium azoimide and liberate nitrogen. When a graphite anode is employed, the ratio averages 0.334, indicating that the N_3^- ions are converted quantitatively into molecular nitrogen. E. G.

Attempt to Prepare Nitro-Nitrogen Trichloride, an Electromeride or Ammono-Nitrogen Trichloride. WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1913, 35, 767-775).—Noyes and Lyon (A., 1901, ii, 601) have shown that the primary reaction between ammonia and chlorine yields nitrogen trichloride and nitrogen, and have suggested that in the course of the reaction the chlorine molecules may split up into Cl^+ and Cl^- ions, and that some of the N and H atoms are temporarily positive and others negative.

It has also been observed that when nitrogen trichloride is titrated with arsenious acid solution, one molecule of the trichloride is equivalent to six atoms of available chlorine. This indicates that the nitrogen of the compound is negative and the chlorine positive, and that it hydrolyses as a reversible reaction:



It then occurred to the author that there might be another nitrogen trichloride, in which the nitrogen would be positive and the chlorine negative, and which would hydrolyse normally, thus:



In this case, the two nitrogen trichlorides might be termed ammono-nitrogen trichloride and nitro-nitrogen trichloride respectively.

Attempts to prepare nitro-nitrogen trichloride have been made by passing a mixture of nitrosyl chloride and phosphorus pentachloride through a strongly heated porcelain tube. No appreciable amount of the trichloride was obtained, but evidence of its existence was secured, and an analysis of the products of the reaction showed that the compound indicated could not have been the ammono-nitrogen trichloride. E. G.

The Solid Hydrogen Phosphides. LOUIS HACKSPILL (*Compt. rend.*, 1913, 156, 1466-1468).—The four alkali phosphides having the general formula M_2P_3 (compare Hackspill and Bossuet, A., 1912, ii, 252), when treated with very dilute acetic acid, give a hydrogen phosphide in the form of a yellow solid, the composition of which corresponds with H_2P_3 . Further, the solid phosphide obtained by Stock, Böttcher, and Lenger (compare A., 1909, ii, 727), when heated in a vacuum at 80°, loses a considerable amount of gaseous phosphide, and after several hours the compound H_2P_3 is left behind. This substance is of an acid nature, since it furnishes metallic phosphides with corresponding formulae, K_2P_3 , Rb_2P_3 , etc. W. G.

Crystallisation of Carbon Dioxide, Nitrous Oxide, and Ammonia. H. E. BEHNKEN (*Jahrb. Min.*, 1913, i, Ref. 182; from *Physical Review*, 1912, 35, 66-73).—These substances were

crystallised on the stage of the microscope with the aid of liquid air. All of them belong to the cubic system, and carbon dioxide was obtained as good, clear, optically isotropic crystals, showing the cube and octahedron.

L. J. S.

A Simple Method for the Preparation of Argon; Chemical Activation of Diatomic Gases in the Glow Discharge.

JOHANNES STARK (*Physikal. Zeitsch.*, 1913, 14, 497—498).—The author has observed that when oxygen from a cylinder (prepared by the fractionation of liquid air) is led into a tube through which canal rays are passing, and in which mercury vapour is also present, the oxygen rapidly disappears; the walls of the tube become coated with a deposit of mercuric oxide and mercuric nitrite, and argon, which was contained in the oxygen, is left behind. The spectrum shows the lines of mercury and argon; even the strongest lines of oxygen are very weak, whilst those of nitrogen are absent.

A ready method is thus given for obtaining small quantities of argon in a short time, and the author describes a simple piece of apparatus for carrying out such a process.

The ready combination of the mercury vapour with the oxygen and nitrogen is supposed to be due to the dissociation of the diatomic molecules into their atoms under the influence of the discharge; the atoms are then very active chemically. It is further shown that when submitted to the glow discharge, oxygen readily combines with aluminium, and hydrogen reduces mercuric oxide below 100°, etc.

T. S. P.

Reduction of Some Volatile Halogen Compounds with Potassium Powder. ALEXANDER C. VOURNASOS (*Zeitsch. anorg. Chem.*, 1913, 81, 364—368).—Pure phosphorus trichloride and similar compounds do not react with massive potassium when cold, but reaction is readily brought about by dissolving the halogen compound in toluene, and using the potassium in the form of dust, obtained by shaking vigorously in hot toluene. The potassium must be freshly prepared in the required quantity for each experiment. Phosphorus trichloride is thus completely reduced, according to the equation $\text{PCl}_3 + 6\text{K} = 3\text{KCl} + \text{K}_3\text{P}$, and by adding a little glacial acetic acid to the product, gaseous, non-inflammable hydrogen phosphide may be obtained. Phosphorus bromide and iodide behave similarly.

Arsenic trichloride yields metallic arsenic, but no arsenide, and this is also the behaviour of antimony and bismuth. The chlorides of carbon and silicon are not acted on at the temperature of boiling toluene. Tin tetrachloride yields finely divided metallic tin. Boron trichloride is only slowly reduced, yielding amorphous boron; the bromide somewhat more readily. Titanium tetrachloride yields partly the dichloride and partly titanium.

Potassium amalgam is much less active than the powdered metal.

C. H. D.

Alcoholic Potassium Hydroxide. RUDOLF GAZE (*Chem. Zentr.*, 1913, i, 1361; from *Apoth. Zeit.*, 1913, 28, 174).—The author claims that alcoholic potassium hydroxide made by his method (A., 1911, ii, 225) will keep colourless much longer than the solution prepared according to Malfatti (A., 1911, ii, 979).

J. C. W.

Temperature-Concentration Diagrams of Potassium Sulphate with the Sulphates of the Alkaline Earths and of Lead, with Reference to the Dimorphism of Anhydrite, Celestine, Barytes, and Anglesite. WERNER GRAHMANN (*Zeitsch. anorg. Chem.*, 1913, 81, 257–314).—Calcium sulphate may be melted in an electric furnace without decomposition, and gives the freezing point 1450° , and transformation point 1193° . The following transformation points are also observed: strontium sulphate, 1152° ; barium sulphate, 1149° ; lead sulphate, 852° .

A special form of heating microscope is described for the optical determination of transformation temperatures. Anhydrite, celestine, barytes, and anglesite pass into α -modifications, probably monoclinic, at the transition temperature.

Potassium and glucinum sulphates form a single compound, $K_2SO_4 \cdot 2GdSO_4$, with a maximum m. p. about 910° . Solid solutions are not formed. The compound is tetragonal, and the eutectic with potassium sulphate is fine-grained and sometimes radiating. The system potassium sulphate-magnesium sulphate has been examined by Nacken (A., 1908, ii, 692), whose results are confirmed. Solid solutions are formed to a limited extent at the potassium end of the series. The diagram of the system potassium sulphate-calcium sulphate differs in several respects from that given by Müller (A., 1910, ii, 776). α -Potassium sulphate retains up to 18 mol. % $CaSO_4$ in solid solution at high temperatures, but the solubility diminishes with falling temperature, and disappears at the transformation temperature. The compound $K_2SO_4 \cdot 2CaSO_4$ decomposes into β -calcium sulphate and liquid at 1004° , and undergoes a polymorphic change at 938° . There are thus three breaks in the ascending branch of the freezing-point curve. The diagram of the system potassium sulphate-strontium sulphate is entirely similar. The limits of solid solution at the eutectic temperature are 0–22 mol. % $SrSO_4$, and the compound $K_2SO_4 \cdot 2SrSO_4$ is resolved into liquid and β - $SrSO_4$ at 980° , and undergoes a transformation at 775° . The system potassium sulphate-barium sulphate is so far different that no evidence of a compound is formed. The first branch of the freezing-point curve, representing the solidification of solid solutions, passes through a maximum at 1087° . The limit of saturation is 24 mol. % $BaSO_4$, and, as before, the β -modification does not form solid solutions.

In the system potassium sulphate-lead sulphate, solid solutions are formed up to 27 mol. % $PbSO_4$, diminishing with falling temperature. The compound $K_2SO_4 \cdot 2PbSO_4$ has a maximum m. p. 942° , and is dimorphous, with a transformation point at 544° . In addition to this, a compound, $K_2SO_4 \cdot PbSO_4$, is formed at 619° by a

reaction in the solid state. A number of regularities among the systems considered are pointed out.

C. H. D.

Reciprocal Behaviour of Alkali Sulphates, Chromates, Molybdates, and Tungstates at Low and at High Temperatures.

III. MARIO AMADORI (*Atti. R. Accad. Lincei*, 1913, [v], 22, i, 609—616. Compare this vol., ii, 512).—The curve of crystallisation of the system K_2SO_4 - K_2WO_4 is continuous; there is a slight minimum 10° below m. p. of the tungstate. The transformation point of the tungstate is not visible in mixtures containing more than 15 mol. % of sulphate. The transformation point of the sulphate followed a curve descending to 482° for mixtures containing 50 mol. %, below which point it is no longer visible.

In the system K_2CrO_4 - K_2WO_4 the curve is also continuous, and it is intermediate between the m. p. of the two salts. The transformation points follow curves rising to the transformation points of the pure salts, but were not observable for the mixtures between 15% and 40% of chromate.

The curve of the system K_2MoO_4 - K_2WO_4 is almost a straight line intermediate between the m. p. of the two salts. Here also the transformation points are only observable in mixtures rich in one or other constituent.

The author has also made experiments with potassium dichromate, potassium dimolybdate, and potassium ditungstate. Potassium dimolybdate has m. p. 484° , potassium ditungstate has m. p. 555° . Neither salt shows any transformation point. The curves of the three systems formed by taking pairs of these salts are continuous, and are very similar to those of the corresponding normal salts.

R. V. S.

Potassium and Sodium Chromates; Mixed Crystals and Double Salt; Relation to the Corresponding Sulphates.

E. FLACH (*Jahrb. Min.*, 1913, i, Ref. 212; from *Inaug. Diss. Leipzig*, 1912).—Solubility determinations and thermal curves indicate the existence of the double salt $3K_2CrO_4 \cdot Na_2CrO_4$ ("chromglaserite," corresponding with the sulphate glaserite). This rhombohedral double salt is capable of forming mixed crystals to a limited extent with sodium chromate. Fused mixtures on cooling give at first hexagonal mixed crystals, which during the transformation interval of 669 — 371° mostly split into the simple chromates and mixed crystals of chromglaserite and sodium chromate. The topic axes of the isomorphous simple chromates and sulphates and of the double salts are compared.

L. J. S.

The Error Due to Salts in the Colorimetric Measurement of Hydrogen Ion Concentration in Sea-water. SÖREN P. L. SÖRENSEN and SVEN PALITZSCH (*Biochem. Zeitsch.*, 1913, 51, 307—313. Compare A., 1910, ii, 404).—The necessary corrections, plotted in the form of curves, are given for borate mixtures and phenolphthalein, borate mixtures, and naphtholphthalein, and phosphate mixtures and naphtholphthalein.

S. B. S.

Complex Citrophosphate Salts. ALFREDO QUARTAROLI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 511—512).—Polemical. The author considers not only that his work has not been recognised by Pratolongo in the publications of this author, but also that the existence of complex ions in citrophosphate solutions (Quartaroli, A., 1911, ii, 489) is demonstrated by the experiments of Pratolongo himself (this vol., ii, 282, 467). R. V. S.

Binary Systems of Lithium Chloride with the Chlorides of the Alkali Earth Metals. CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 629—636. Compare this vol., ii, 137).—Lithium chloride and magnesium chloride form in all proportions solid solutions, which are also stable at low temperatures. The curve shows a minimum corresponding with 40 mol. % of $MgCl_2$ and 570° .

Lithium chloride and calcium chloride give a continuous series of solid solutions, which crystallise along a curve having a very acute minimum corresponding with 36.4 mol. % of $CaCl_2$ and 492° . Mixtures between 10 mol. % and 60 mol. % of $CaCl_2$ show an evolution of heat after solidification, and the curve indicates that the solid solutions break up at a temperature very near that of crystallisation, yielding a mechanical mixture of two solid solutions containing the components in very limited proportions.

With strontium chloride and with barium chloride, lithium chloride yields simple eutectics. The eutectic in the case of strontium chloride corresponds with 48 mol. % of $SrCl_2$ and 492° , whilst in the case of barium chloride the eutectic lies at about 33 mol. % of $BaCl_2$ and 510° . R. V. S.

Anhydrous Condition and Stability of Fused Lithium Perchlorate and Their Bearing on the Atomic Weight of Silver. THEODORE W. RICHARDS and MARSHALL W. COX (*Chem. News*, 1913, 107, 267—268).—In their work on the atomic weights of silver and lithium Richards and Willard (A., 1910, ii, 292) weighed lithium perchlorate, which had been fused and dried at 300° . This procedure involved two possible sources of error: (1) the retention of traces of moisture by the salt, (2) slight decomposition of the salt. The chlorate or chloride resulting from (2) could easily be detected, but the investigation of (1) is difficult. It is now shown that lithium perchlorate treated as described loses no appreciable trace of water when heated to 400° (when slight decomposition occurs) or to 430° (when much oxygen is given off). It is possible, however, that traces of water may be held by the salt in the form of lithium hydroxide, and this point is still under investigation. T. A. H.

The Behaviour of Ammonium and Alkali Nitrates and Nitrites, and also of the Corresponding Salts of Some Substituted Ammonium Compounds Towards Reducing Agents WILHELM VAUBEL (*Chem. Zeit.*, 1913, 37, 637—638. Compare Kaufmann, A., 1901, ii, 554).—In order to accelerate the expulsion

of nitric acid from solutions before precipitation with hydrogen sulphide, the author's students added ammonia, and then heated. It was found that in spite of long heating considerable quantities of combined nitric acid remained behind; in spite of this, however, after acidifying with hydrochloric acid no precipitate of sulphur was produced with hydrogen sulphide. Further experiments showed that mixtures of ammonium chloride and nitric acid, and of ammonium nitrate and nitric acid were reduced by hydrogen sulphide, whereas one of ammonium nitrate and hydrochloric acid was not, unless the acid was concentrated. This is apparently not in agreement with the law of mass action.

The above observations led to further experiments on the action of other reducing agents on ammonium nitrate and nitrite. The ordinary metals, with the exception of iron, reduce ammonium nitrate to nitrite. With iron the reduction generally gives ammonia without the intermediate formation of nitrite, although in some cases nitrite was detected; at the same time a small portion of the iron dissolves, giving a complex compound in which the iron may be in the ferrous, ferrous-ferric, or ferric condition.

The intermediate formation of nitrite occurs in the action of iron on aniline and *p*-toluidine nitrates, alkali nitrates, and calcium nitrate.

Neutral solutions of ammonium, potassium, and sodium nitrites, have no action on iron in the cold; the latter also have no action, or only a very slow one, when hot.

T. S. P.

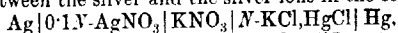
Modifications of Silver. III. Silver from Solid Compounds.

VOLMAR KOHLSCHÜTTER and E. EYDMANN (*Annalen*, 1913, 398, 1—48. Compare A., 1912, ii, 253, 845).—A substance changing by molecular decomposition to a more highly condensed state appears to be in a condition of molecular plasticity, since the appearance of the final product is markedly affected by material and physical factors operating during its formation. Silver is a substance in which the property is particularly pronounced. The hair and mirror modifications of silver have already been described (*loc. cit.*). The present communication deals with the appearance and properties of silver produced from its solid compounds either by direct decomposition or by interaction with another substance. External factors, such as the temperature and so forth, and, as far as possible, the course of the reactions have been studied, since without a knowledge of these conditions the production of different modifications is not intelligible. The preparation and the decomposition of silver oxide, carbonate, oxalate, azoimide, hyponitrite, and nitrite are described. Many interesting facts are stated, but in a form unsuitable for abstraction. Mention may be made, however, of the facts that the decomposition of the carbonate is endothermic and of the oxalate exothermic; also that a certain amount of silver nitrate is produced during the decomposition of the nitrite and hyponitrite. Since amorphous silver becomes crystalline by heating under fused silver nitrate, the production of this salt during the last two decompositions accounts for the presence of a little crystallised silver in

the products of these decompositions; in all other cases the silver is amorphous.

A remarkable fact has been observed in connexion with the decomposition of silver carbonate. Silver oxide, heated in a vacuum, decomposes most favourably at 320°. Silver carbonate decomposes rapidly in a vacuum at 216°. If the gas (carbon dioxide) is pumped off, the product can be heated to 320° without any further evolution of gas. When, however, the product is allowed to cool and is then reheated, a rapid evolution of gas occurs at 235° and the decomposition of the oxide then proceeds normally. The reduction of silver oxide by hydrogen at about 70° and finally at 100—120° is described, as also its reduction by partly dried carbon monoxide at the ordinary temperature; the reduction of silver oxide by dry carbon monoxide only commences at about 100°. Finely divided silver has also been prepared from silver chloride by Wislicenus's method of reduction with zinc and dilute sulphuric acid, by Stas' method with aqueous potassium hydroxide and lactose, and by Vanino's method with sodium hydroxide and formaldehyde. Aqueous silver nitrate has also been reduced by sulphur dioxide. This silver is crystalline; silvers obtained by the other methods are amorphous, and differ from one another distinctly in colour, lustre, friability, and size of the particles.

The isolation of silver in such different forms is the reason for the frequently expressed view that the metal occurs in allotropic modifications. Now, the essential difference between allotropes is the difference in the energy-content. This difference has been measured by various observers by different methods, the results of which lead to the inference that silver does exist in allotropic modifications. The authors, however, are of opinion that the quantitative differences in the energy-content of various modifications of silver are due, not to allotropy, but to the difference in the size of the particles, being conditioned by surface-energy. Employing the various modifications of silver mentioned above, they have examined the reduction of ferric alum in dilute sulphuric acid by silver, and find that the equilibrium constant between the ferric, ferrous, and silver ions is, for the different modifications, not sufficiently different to justify the inference that the modifications are allotropic. This conclusion is supported by measurements of the potential between the silver and the silver ions in the cell,



and by determinations of the density of the different modifications of silver in a Muthmann pyknometer containing benzene.

Since Bredig and Teletov have shown that the velocity of the catalytic decomposition of hydrogen peroxide by platinum is proportional to the active surface of the metal, the authors have attempted to verify their opinion that the differences in the energy-content of the various modifications of silver are due to differences in the surface energy by measuring the velocity of the decomposition of hydrogen peroxide in the presence of silver, either by the diminution of the potassium permanganate titre, or, better, by measuring the volume of oxygen evolved. The various modifications of silver

exhibit quantitative differences in their catalytic activity; silvers obtained by the formaldehyde reduction or from the oxide by means of carbon monoxide or hydrogen are the most, and about equally, active.

A description is given of experiments in the sintering or shrinking of silver by heating. For a given modification the shrinking is the same whether the silver is heated slowly or suddenly, but the shrinking of the various modifications of silver is very different; silver powder prepared by wet processes begins to sinter noticeably at 200° , whilst powders prepared by dry processes only begin to shrink appreciably at 300° .

C. S.

Electrolytic Preparation of Calcium and Calcium Alloys.

WILHELM MOLDENHAUER and J. ANDERSEN (*Zeitsch. Elektrochem.*, 1913, **19**, 444—447).—Starting from the fact that at high temperatures potassium is more electropositive than calcium (Danceel and Stockem, A., 1905, ii, 388), the authors have carried out experiments with the object of preparing metallic calcium from molten mixtures of calcium and potassium chlorides. They first determined the melting-point curve of mixtures of the two chlorides, and find a maximum at 740° which lies between two minima both at 630° . The maximum melting point occurs for a mixture of equal molecules of the two chlorides, and is stated to represent the melting point of KCaCl_3 , whilst the minima occur at the compositions 85% CaCl_2 and 40% CaCl_2 ; the former is the eutectic point for CaCl_2 and KCaCl_3 , whilst the latter is the eutectic point for KCl and KCaCl_3 .

The first electrolyses were for the purpose of preparing calcium alloys which should contain no potassium. A mixture of 85% CaCl_2 and 15% KCl was placed in an iron crucible which served as the cathode, a graphite rod being used as anode. The mass was melted by the current and a quantity of zinc added; this melted, and formed eventually the cathode. In this way calcium zinc alloys were obtained containing up to 67% calcium which were absolutely free from potassium. In a similar manner lead calcium alloys were obtained up to 81.9% calcium. Pure calcium itself was prepared from a mixture of 85% CaCl_2 and 15% KCl , using the Rathenau method, the current density being 60—110 amperes per sq. cm. The metal was practically free from potassium, and the current efficiency varied between 75% and 90% of the theoretical. Experiments with 40% CaCl_2 and 60% KCl did not give a coherent stick of calcium as in the other cases, probably due to separation of potassium and the high melting point of the alloy. J. F. S.

Action of Silver Salts and Colloidal Metals on Lumino-phores. IV. LUDWIG VANINO and PAULA SACHS (*J. pr. Chem.*, 1913, [ii], **87**, 508—512. Compare A., 1909, ii, 731; 1910, ii, 847; 1911, ii, 885).—The authors have investigated the effect of the addition of traces of silver nitrate on the luminosity of the phosphorescent sulphide mixtures previously described, and find that although in some instances the addition produces an increased

luminosity, this is not universally the case, the silver nitrate often having little or a deleterious effect.

In the preparation of the phosphorescent stones, colloidal metals may be used with advantage in the place of the nitrates hitherto employed; thus the replacement of silver and bismuth nitrates by colloidal solutions of the metals is accompanied in many instances by an increase in the luminosity.

F. B.

Calcium Boride. EDGAR WEDEKIND (*Ber.*, 1913, 46, 1885—1889).—Calcium metaborate (30 grams), when reduced by means of calcium (50 grams) in the author's apparatus (this vol., ii, 225), gives rise to the theoretical quantity of calcium boride, CaB_2 , which has been obtained previously by Moissan in an impure condition. The reaction product is extracted with dilute acetic acid and then dilute hydrochloric acid, and finally washed with hot water. It forms a fine, light brown, microcrystalline powder, $D^{20}_D = 2.11$, and is a conductor of electricity. If two electrodes are made by compressing the powder, and an arc struck between them, the chief mass sinters together, giving a product which cuts glass. On heating in the air, superficial oxidation to borate takes place. Other chemical properties are as given by Moissan.

Experiments to obtain barium boride from barium borate and calcium were not successful, the product always containing calcium.

T. S. P.

Pozzuolana. GIOVANNI GIORGIS and GINO GALLO (*Gazzetta*, 1913, 43, i, 353—361. Compare Gallo, A., 1908, ii, 844).—It was observed (*loc. cit.*) that when lime-water acts on pozzuolana the substance swells up into a flocculent mass, which is the object of chemical investigation in this paper. The experiments were carried out with material from S. Paolo and Pratolungo (which are typical Roman pozzuolane) and from Bacoli. The mucilaginous substance was obtained by treating the pozzuolana with lime-water for six months with frequent stirring, and the results of its analysis are given in two tables. The behaviour of the two first-named materials was similar, but the Bacoli product gave a greater residue insoluble in hydrochloric acid and in potassium hydroxide, and this agrees with the fact that this pozzuolana sets more slowly. The results indicate a tendency to the formation of definite compounds in the reaction, but the small amount of calcium found in the gummy product as compared with the quantity of silicon and aluminium, indicates that the action is far from complete after the period of the experiment. The residue insoluble in hydrochloric acid and in potassium hydroxide differs in composition from the original pozzuolana.

The authors reply to criticisms by Manzella (A., 1912, ii, 352).

R. V. S.

Technical Preparation of Baryta. I. LUIGI MARINO (*Gazzetta*, 1913, 43, i, 416—422).—This paper forms the introduction to a series of researches undertaken with the object of simplifying the

technical preparation of baryta, so as to reduce its cost and make it more available for the treatment of molasses. The author finds that the reduction of barium sulphate to barium sulphide is effected by reducing gases better than by coal, which is generally employed at present. The reduction with hydrogen, methane, water gas, illuminating gas, etc., occurs at about the same temperature, as these gases inflame with oxygen, and the temperature of reduction can be lowered by the aid of suitable catalysts, just as combination with oxygen can be favoured by the same means. For commercial purposes the best results are obtained with water-gas, the reduction occurring at 525—540°. In practice a temperature of 600—625° is employed.

R. V. S.

Technical Preparation of Baryta. II. Reduction of the Sulphates of the Alkaline Earths with Different Gases. LUIGI MARINO and D. DANESI (*Gazzetta*, 1913, 43, i, 423—434. Compare preceding abstract).—The authors have investigated the reduction of the sulphates of barium, calcium, and strontium with each of the gases: hydrogen, methane, carbon monoxide, water gas, and illuminating gas. The reduction was effected by passing the gas over the sulphate contained in a boat placed in a porcelain tube. The tube could be heated electrically. The temperature was measured with a platinum, platinum-rhodium couple, and the beginning of the reduction was taken to be indicated by the first appearance of traces of hydrogen sulphide or of carbon dioxide in the issuing gas; at a somewhat higher temperature the formation of water is visible. In all cases the reduction is complete at temperatures a little above those at which the water makes its appearance. In the case of barium sulphate the product of reduction is always the sulphide; strontium sulphate yields sulphide with traces of oxide and thiosulphate, whilst from calcium sulphate, sulphide and small quantities of oxide and thiosulphate are also obtained. The temperature of reduction is different for the different gases, and has intermediate values for mixtures of gases; it is lowest for barium sulphate, higher for strontium sulphate, and highest for calcium sulphate.

R. V. S.

Technical Preparation of Baryta. III. Rotatory Furnace for the Continuous Production of Barium Sulphide by Reduction of the Sulphate with Gaseous Substances. LUIGI MARINO and D. DANESI (*Gazzetta*, 1913, 43, i, 434—439. Compare two preceding abstracts).—The essential part of the furnace consists of an iron tube covered externally by a porcelain tube, which is provided with a nickel spiral for electrical heating, the whole being jacketed with magnesia. The tube and its covering are rotated at any desired speed, and are also inclinable to any desired, fixed angle. The barium sulphate is fed into the tube from a hopper at the upper end, and the sulphide falls into a receptacle connected with the other end, the inclination and speed of the tube being so adjusted that the sulphate stays in the tube long enough to be reduced completely (about one hour at 600—650°). The

reduction is effected with water-gas, which is passed into the tube from the lower end. The yield of sulphide is 95—98%. R. V. S.

Metallic Glucinum. FRITZ FICHTER and KASIMIR JABLONZYNSKI (*Ber.*, 1913, 46, 1604—1611).—Glucinum is best obtained by the electrolysis of a fusion containing 1 mol. of sodium fluoride to 2 mols. of glucinum fluoride (compare Lebeau, A., 1898, ii, 511), using a nickel crucible as cathode, a carbon rod anode, and a current strength of 7—10 amperes at 15 volts. The temperature must not rise too high, otherwise an alloy of glucinum and nickel is formed. The metal is isolated from the fusion by dissolving the salts in water, the solution being prevented from becoming acid by the addition of ammonia and by repeated renewal of the water. The crystals of glucinum so obtained are freed from admixed oxide by centrifugalisation in a mixture of ethylene dibromide and alcohol ($D\ 1.95$); they have $D=1.842$. The small crystals so obtained cannot be melted together under ordinary conditions, owing to the coating of oxide formed preventing coalescence; it is necessary to form cylinders by compression, and then heat them up in an electric vacuum furnace, or in one containing hydrogen at 11—15 mm.

The m. p. is $1280^{\circ} \pm 20^{\circ}$. The regulus of metal has hardness between 6 and 7, and scratches glass; the freshly-filed metal is steel-grey in colour. At the ordinary temperature it is brittle, but at higher temperatures ductile. The specific electrical conductivity is 5.41×10^4 reciprocal ohms.

The resistance to the action of water is caused by a surface film of oxide. As anode in a solution of sodium ammonium phosphate it acts as a rectifier, similarly to aluminium. It is not so readily attacked by alkalis as is usually stated to be the case. T. S. P.

Compounds of Arsenious Acid with Glucinum. BENNO BLEYER and BR. MÜLLER (*Arch. Pharm.*, 1913, 251, 304—319. Compare A., 1912, ii, 644; this vol., ii, 137).—It was found to be impossible to prepare definite compounds of arsenious acid with glucinum, and consequently the behaviour of a colloidal precipitate (gel) of glucinum hydroxide with solutions of arsenious anhydride in water was investigated. It was found that when using even freshly prepared glucinum hydroxide (10 grams of precipitate = 0.6349 gram GIO) only very small amounts of the arsenious anhydride were absorbed, due probably to the rapidity with which the precipitated hydroxide loses its colloidal character. With glucinum hydroxide precipitated by ammonia and ammonium chloride in the arsenious solution larger quantities of the anhydride were absorbed at the ordinary temperature, and these were absorbed in accordance with the adsorption law. At the temperature of boiling water the quantities absorbed were less than at the ordinary temperature, and followed Henry's law, that is, the relation between the quantity of arsenious anhydride absorbed and that remaining in the solution was constant. T. A. H.

Electrometallurgy of Zinc. GINO GALLO (*Gazzetta*, 1913, 43, i, 361—385).—Reviewing the methods employed in the metallurgy of zinc, the author points out that electrolysis is not successful because, when zinc chloride is employed, it is necessary either to obtain the absolutely anhydrous salt or to electrolyse for a long period before the separation of metallic zinc begins. He finds, however, that these difficulties can be overcome by employing zinc fluoride instead of the chloride. Anhydrous zinc fluoride is readily prepared by heating for two hours at 125° either the hydrated fluoride or the silicofluoride. When the anhydrous salt is heated, it reacts with the water vapour of the flame below its m. p. (734°), yielding hydrogen fluoride and zinc oxide. If, however, it is previously mixed with an equal amount of sodium chloride, or even with half that quantity, the m. p. is lowered to about 500° and fusion is readily effected. When the fused mixture is electrolysed, a very small current is sufficient to cause the immediate separation of shining globules of metallic zinc, whilst if zinc oxide is added to the fused mass from time to time, only oxygen is evolved at the positive pole, a tension of 3 volts being employed. Details are given of a large-scale process founded on this method, using blende or calamine. The previous removal of the iron of the ores is desirable, for if this is not done the iron accumulates in the electrolysing vessel. The removal can be effected by magnetic selection, or by a new method here described, which consists in treating roasted blende or natural calamine with hydrofluosilicic acid. A pure solution of zinc silicofluoride is thus obtained, whilst all the iron is precipitated as ferric hydroxide. If the solution is evaporated and the residue heated at 150° , the zinc salt decomposes, leaving zinc fluoride. The silicon fluoride evolved is collected and used again.

R. V. S.

Zincoso-zincic Chloride. RASIK LAL DATTA and HARIDAS SEN (*J. Amer. Chem. Soc.*, 1913, 35, 779—780).—Zincoso-zincic chloride, Zn_3Cl_5 or $\text{ZnCl}_2 \cdot 2\text{ZnCl}_2$, obtained by the gradual addition of zinc to fused zinc chloride until it ceases to be dissolved, is a bluish-white, hygroscopic solid, and is rapidly hydrolysed by water. The study of this compound is being continued, and attempts are being made to prepare zincous chloride, ZnCl .

E. G.

Etched Figures of Crystals of Zinc Ammonium Sulphate. N. I. SURGUNOV (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 405—406).—The etched figures of crystals of zinc ammonium sulphate, $\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, show the symmetry to be expected from holohedral forms of the monoclinic system (compare Tutton, T., 1905, 1140).

T. H. P.

Arsenic Compounds of Cadmium. SERGEI F. SCHEMITSCHUSCHNY (*Intern. Zeitsch. Metallographie*, 1913, 4, 228—247).—The freezing-point curve of the alloys of cadmium and arsenic, which has been determined as far as 70 atomic % As, has two maxima, corresponding with the compounds Cd_3As_2 , m. p. 721° , and

CdAs_2 , m. p. 621° , respectively. The formation of the latter compound is readily suppressed by undercooling, so that the descending branch of the Cd_3As_2 curve may be followed as far as a metastable eutectic point at 526° . The compound Cd_3As_2 has a polymorphic transformation point at 578° . The normal eutectic points are at 319° , close to the freezing point of cadmium and at 610° . Solid solutions are not formed to an appreciable extent, and there is no indication of the formation of a compound, CdAs , even after prolonged heating of the solid alloys. The structure of alloys rich in arsenic varies greatly with the presence or absence of inoculation.

The compound Cd_3As_2 is grey with a red shade, whilst CdAs_2 is very dark grey with a blue shade.

The atomic-volume curve consists of three straight lines, with well-marked breaks at the composition of the two compounds. Both compounds are formed from their components with considerable expansion. Cd_3As_2 has D 6.25 and CdAs_2 D 5.86. The latter compound is harder than either component.

C. H. D.

Solid Solutions of Compounds of Calcium, Strontium, Barium, and Lead with those of the Rare Earths. I. FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1913, [v], 22, 1, 519—524).—The author proposes to ascertain the existence of solid solutions of the types mentioned, because it is assumed in the explanation of the composition of some important minerals containing the rare earths. The present paper gives the results obtained by the method of thermal analysis in the case of the system $\text{PbWO}_4\text{--Ce}_2(\text{WO}_4)_3$. The m. p. of cerium tungstate is 1089° , that of lead tungstate 1125° . The two substances are miscible in all proportions, both in the liquid and in the solid state, and the curve shows no thermal effect at any point.

R. V. S.

Metallurgy of Copper as Carried Out in Ancient Times in the Lands which are Populated by Rumanians at the Present Time. C. NICOLSCU-OTIN (*Bull. Sci. Acad. Roumaine*, 1912-3, 1, 297—302).—The author has analysed various prehistoric articles made of copper, or of copper and tin, and also various Roman articles made respectively of copper, lead, and zinc; copper, lead, and tin; and copper, lead, tin, and zinc. Comparison of the impurities present in these articles with the impurities present in the Rumanian ores of the present day, lead him to the conclusion that the metals used were obtained from the local ores. Apparently the prehistoric metallurgists could smelt copper almost as well as the Romans, since their products contained at times as much as 99% copper.

T. S. P.

Cupric Iodate. JAMES F. SPENCER (*Zeitsch. physikal. Chem.*, 1913, 83, 290—296).—The preparation of cupric iodate is described, and the action of heat and its solubility in water and solutions of potassium iodate and copper sulphate of varying concentrations determined. The solubility is determined by measuring the ionic

concentration of both ions by means of electrodes of the second and third types. The electrode for measuring the iodate ion is described (A., 1912, ii, 1129). An electrode of the third type is described for the measurement of cupric ions; it has the form $\text{Hg}|\text{Hg}_2(\text{IO}_3)_2|\text{Cu}(\text{IO}_3)_2|\text{Cu}^{++}$ and the value $\epsilon = 0.6060 + 0.0297 \log \text{Cu}$ at 25° . The solubility of $\text{Cu}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ at 25° is 3.30×10^{-3} gram mols. per litre, and it is depressed normally by the addition of either copper sulphate or potassium iodate to the solution, without the formation of complexes. Cupric iodate loses its water of crystallisation at 240° , but only takes it up again very slowly even when placed in water. J. F. S.

New Method for the Preparation of Ammoniacal Copper Salts. KSHITIBHUSHAN BHADURI (*Zeitsch. anorg. Chem.*, 1913, 81, 406–408. Compare this vol., ii, 53).—Powdered cupric oxide is rubbed with concentrated ammonia until dissolved; the ammonium salt of the required acid is then added, and the rubbing continued until solid salt separates.

Ammonical cupric thiocyanate, $\text{Cu}(\text{CNS})_2 \cdot 4\text{NH}_3$, forms blue crystals, which lose first 2 and then 3NH_3 . Ammoniacal cupric ferricyanide, $\text{Cu}_3[\text{Fe}(\text{CN})_6]_2 \cdot 6\text{NH}_3$, prepared from ammoniacal cupric hydroxide and potassium ferricyanide, forms black crystals, and is very stable. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{NH}_3 \cdot 2\text{H}_2\text{O}$ is stable in air. $\text{CuL}_2 \cdot 6\text{NH}_3$ is blue and unstable. C. H. D.

The Sulphate-tensions and Affinity of the Rare Earths. LOTHAR WÖHLER and M. GRÜNZWEIG (*Ber.*, 1913, 46, 1726–1732).—The sulphate-tensions of the rare earths have been measured (compare A., 1908, ii, 290) over a range of temperatures varying from 800 to 1020° , in order to obtain a measure of their affinity, that is, of their basic character. The following table shows the order in which the earths arrange themselves according to the value of the partial pressure (in mm. of mercury) of sulphur trioxide (P^{SO_3}) over their sulphates at 900° , and also the heat of dissociation (Q), calculated according to Nernst's theorem:

Metal...	Sc.	Sa.	Gd.	Nd.	Pr.	Er.	Yb.	Lu.	Yt.	La.
P^{SO_3}	11	8	7	6	5.5	5	4	3.5	3	2
Q (Cal.) ...	54.5	56.6	56.9	57.2	57.4	57.6	58.2	58.5	58.9	59.8

These figures show that the rare earths belong to the strongest bases; the heats of dissociation are the greatest hitherto observed for trivalent sulphates. The above order is, however, different from that which has hitherto been assumed, namely, Sc, Yb, Er, Gd, Sa, Y, Ce^{III} , Nd, Pr, La.

The basic sulphates of the above elements are readily obtained by heating the sulphates in the air at 800 – 850° ; *basic neodymium* and *praseodymium sulphates* both conform to the general formula: $\text{R}_2\text{O}_3 \cdot \text{SO}_3$.

The tension curves run almost parallel and very close to each other, the horizontal difference between them, measured in degrees centigrade, being small. This means that it would be more or less difficult to separate two sulphates from each other by heating them

to a constant, intermediate temperature at which one gives the basic sulphate and the other remains undecomposed and soluble in water. An example is given, however, of the separation of an artificial mixture of neodymium and praseodymium sulphates by this means.

T. S. P.

Copper-Aluminium Alloys with 84 to 90% of Copper. H. HANEMANN and P. MERICA (*Intern. Zeitsch. Metallographie*, 1913, 4, 209—227).—A close analogy is observed between the structure of these alloys and that of steel. Quenching from above the eutectoid point gives a martensitic structure in the case of hypoeutectoid alloys. Hypereutectoid alloys, like high carbon steels, yield a homogeneous solid solution when quenched from a sufficiently high temperature, the β -phase in copper-aluminium alloys taking the place of austenite in steels, whilst the γ -phase resembles cementite. The microscopic structures are discussed in detail.

C. H. D.

The β -Constituent of Aluminium Bronzes. A. PORTEVIN (*Intern. Zeitsch. Metallographie*, 1913, 4, 257—260. Compare preceding abstract).—The β -constituent in alloys of copper and aluminium may occur in a cellular or lamellar form, the cellular type predominating in the neighbourhood of primary crystals.

C. H. D.

Crystallographic Investigation of Hydrated Aluminium and Ferric Nitrates. N. I. SURGUNOV (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 407—412).—Nonhydrated aluminium and ferric nitrates deliquesce rapidly in the air at the ordinary temperature. For monoclinic crystals of the aluminium salt, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, which show several faces not observed by Soret (*Arch. Sci. phys. nat.*, 1886, [iii], 16, 460), the author finds $a : b : c = 1.1321 : 1.19174$, $\beta = 131^\circ 32'$; Soret gave $a : b : c = 1.13398 : 1.191913$, $\beta = 131^\circ 36'$.

The ferric salt, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, forms pale red, monoclinic crystals, $a : b : c = 1.1296 : 1.19180$, $\beta = 131^\circ 34'$.

T. H. P.

The System Manganese-Silver. G. ARRIVAUT (*Compt. rend.*, 1913, 156, 1539—1541).—The author has made a thermal study of the system manganese-silver, and the results indicate the existence of a definite compound, MnAg_2 . A microscopic examination of the solidified mixtures of various concentrations in manganese, and a study of the *E.M.F.* of such mixtures against an electrode of silver support this view in opposition to Hindrichs (*A.*, 1908, ii, 856). This compound forms a continuous series of mixed crystals with silver, and its limit of miscibility, in the liquid state, with manganese is about 30% of manganese.

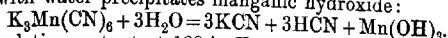
W. G.

A Basic Salt of Manganese Iodide. PETR. KUSNEZTOV (*Chem. Zvesti.*, 1913, i, 1659; from *Izvestia Don. Polytech. Inst. Novotcherkassk*, 1913, 2, ii, 1—7).—When air is passed through a concentrated solution of manganese iodide or when the solution is repeatedly

evaporated, a *basic manganese iodide*, $\text{MnI}_2 \cdot \text{MnO} \cdot 6\text{H}_2\text{O}$, is formed in colourless, microscopic, doubly-refractive needles, which gradually give up iodine at $115\text{--}120^\circ$.

J. C. W.

Tervalent Manganese. I. JULIUS MEYER (*Zeitsch. anorg. Chem.*, 1913, **81**, 385—405).—Potassium manganicyanide is more easily prepared than other manganic salts. For its preparation 400 grams of crystallised potassium cyanide are dissolved in the smallest possible quantity of water, and 100 grams of powdered manganous carbonate are added. Air is then drawn through. At first a blue mass of the manganocyanide, $\text{K}_4\text{Mn}(\text{CN})_6$, is formed, and this oxidises, becoming orange-red. If gently warmed on the water-bath, about a day is necessary for the reaction. The precipitate is collected, washed with alcohol and ether, and dried in air. The reaction is: $2\text{K}_4\text{Mn}(\text{CN})_6 + \text{O} + \text{H}_2\text{O} = 2\text{K}_3\text{Mn}(\text{CN})_6 + 2\text{KOH}$. The salt may be recrystallised from 10% potassium cyanide solution. Boiling with water precipitates manganic hydroxide:



The hydrolytic constant at 18° is $K = 2 \times 10^{-10}$. Concentrated solutions are reddish-yellow, probably owing to the presence of small quantities of manganic cyanide.

Precipitated manganic hydroxide closely resembles ferric hydroxide. It is not altered by shaking with water and air, and is therefore not to be regarded as a mixture of manganous hydroxide and the peroxide. It dissolves in cold concentrated hydrochloric, sulphuric, phosphoric, and hydrofluoric acids, the last three solutions being fairly stable. The double fluoride, K_2MnF_6 , may be isolated in the solid state. Heating converts the hydroxide into the oxide, with partial oxidation.

C. H. D.

Allotropy in General and that of Iron in Particular. CARL BENEDICKS (*J. Iron Steel Inst.*, 1912, **86**, 242—294. Compare Smits, A., 1912, ii, 165, 769, 1058, 1176).—The expansion of silver iodide has been determined in a small apparatus in which the rod of substance is held between two silica rods. From -180° silver iodide has a positive coefficient of expansion, which at -100° is 1.8×10^{-6} , but becomes imperceptible at 0° . From 40° to 140° a gradual contraction occurs, followed by a sudden and very large contraction at about 147° . There is a much larger positive coefficient of expansion above 147° . With rapid heating the contraction from 140° onwards is more gradual, and is only complete at 165° . These results indicate a solubility of the one modification in the other below 147° .

The allotropy of iron is discussed from this standpoint. The point A_{γ_2} is regarded as the mere termination of the A_{γ_1} change. β -Iron is then a solid solution of γ -iron in α -iron, the quantity of the former increasing with the temperature.

C. H. D.

Metallography of Some Ancient Iron Objects. H. HANEMANN (*Intern. Zeitsch. Metallographie*, 1913, **4**, 248—256).—An ancient Celtic tool from Steinsburg, near Röhild, consists mainly

of ferrite and pearlite with slag inclusions, and has been prepared by fusion. The point, however, consists of martensite, and has been hardened in water without subsequent tempering. This is evidence of the great stability of martensite at the ordinary temperature. An axe from the same neighbourhood consists of soft, almost carbonless iron. A Greek faun, dating from the beginning of the Christian era, consists of cast iron containing phosphorus. A Roman discus consists of wrought iron.

C. H. D.

Electrolytic Method for the Prevention of the Corrosion of Iron and Steel. JOHN K. CLEMENT and L. V. WALKER (*J. Ind. Eng. Chem.*, 1913, 5, 361—366).—Results of experiments carried out by the authors show that the corrosion of iron immersed in sulphuric acid may be prevented by the application of a counter E.M.F.; the density of the current required depends on various factors, the more important being acid concentration, amount of dissolved oxygen, and degree of circulation of the electrolyte. The influence of these factors has been investigated, and curves are given showing the current density necessary under various conditions. The current density required can be calculated approximately from the loss in weight of the unprotected metal under given conditions.

W. P. S.

A New Chemical Cause for the Rusting of Iron. WILHELM VAUBEL (*Chem. Zeit.*, 1913, 37, 693—694).—Although nitrates are known to accelerate the action of water on iron, the phenomenon does not appear to have been systematically examined.

Ammonium nitrate is the most effective of this class of salt in attacking iron, and it is very generally present in common water in contact with iron, for this metal will reduce a portion of the dissolved nitrates to ammonia; the same process, namely, the reduction of the nitrate radicle to ammonia, occurs in the action of ammonium nitrate on iron, the latter undergoing oxidation. The rusting is assisted by the increased activity of oxygen at the attacked spot, and also by the action of the water itself, which, it is stated, in the presence of ammonium nitrate will act on iron, forming iron oxide and hydrogen, especially if the temperature is slightly raised. Under ordinary conditions the reduction of nitrate to ammonia by iron occurs without any appreciable formation of nitrite (compare Droste, *Chem. Zeit.*, 1912, 36, 678).

As has already been shown (Bonnema, *Chem. Zeit.*, 1903, 27, 148, 825), ferrous oxide and hydroxide in contact with air give rise to a certain amount of nitrite. If, as is quite possible, nitrate is produced in the same manner, it is clear that for the rusting of iron only a minimal quantity of an ammonium salt need be present, for the ammonium nitrate could then be easily formed.

Ammonium nitrite and nitrites of the alkali metals are almost without any action on iron, as also is ammonium nitrate in alkaline solution. Nitrates of the alkali metals are not nearly so active as ammonium nitrate. The action of the last salt gives rise to ferrous and ferric hydroxides, and also to a certain amount of dissolved

iron, apparently in the form of a complex ion, as the usual reagents do not affect the solution.

D. F. T.

Copper in Steel. The Influence on Corrosion. D. M. BUCK (*J. Ind. Eng. Chem.*, 1913, 5, 447—452).—The steels used were two basic open hearth steels, containing respectively: C, 0·10; Mn, 0·34; S, 0·034; P, 0·019; and C, 0·13; Mn, 0·45; S, 0·036; P, 0·042; and one Bessemer steel containing C, 0·08; Mn, 0·46; S, 0·070; P, 0·092. The amount of copper added was sufficient to give a copper content of either about 0·15 or 0·25%. The steels with and without copper were put through the same mill operations, and were finally obtained as corrugated strips, which were tested for atmospheric corrosion at three different stations: (1) in the Pennsylvania Coke regions, where the air contains notable amounts of sulphurous and sulphuric acids, etc.; (2) on the sea coast; (3) in the country. The strips were put on open sheds and exposed to the atmosphere on all sides, the time of the test lasting for several months; observations were made from time to time.

Full details are given with respect to each test piece. As a general result it may be considered as proved that copper has a very beneficial effect in retarding corrosion; the copper-containing steels resist the atmosphere from one and a-half to two times as well as normal steels without copper, and there is little or no difference in the average between a copper content of 0·15 and 0·30. Accelerated acid tests gave similar results, but it should be pointed out that in some cases the results of the acid tests are directly opposite to the results of the atmospheric tests.

T. S. P.

Influence of Various Elements on the Corrodibility of Iron. CHARLES F. BURGESS and JAMES ASTON (*J. Ind. Eng. Chem.*, 1913, 5, 458—462).—Electrolytic iron, alloyed with various other elements, was used; the test samples were submitted both to acid (20% sulphuric acid for one hour) and atmospheric corrosion, in the latter case for a period of 162 days.

Electrolytic iron showed no special resistance to corrosion, in contradiction to the commonly accepted view that a close approach to purity would indicate a high resistance to acid attack. The other alloys behaved as follows, the added metal being printed in italics: *Aluminium*, 0·067—1·33%. No particular effect. *Arsenic*, 0·29—3·56%. Fair resistance to acid attack, which resistance falls off appreciably with increase in arsenic content. Atmospheric corrosion about the same as for electrolytic iron. *Cobalt*, 1·04—5·05%. Resistance to acid not particularly striking, but falls off appreciably with increasing cobalt content; the same general effect occurs in the atmospheric tests. Effect is not nearly so good as with nickel. *Copper*, 0·089—7·05%. A marked decrease in corrosion (compare preceding abstract). *Lead*, 0·061%. Atmospheric corrosion decreased by one-half, but acid corrosion the same. *Manganese*, 0·50—10·42%. No particular effect, and results inconsistent. *Nickel*, 0·27—75·06%. Good effect, there being a general tendency for increased resistance with increasing content of nickel.

Selenium, 0.017%. Acid resistance very low, and atmospheric corrosion high. *Silicon*, 0.23—2.82%. Corrosion generally high. *Silver*, 0.28—0.69%. Behaviour similar to electrolytic iron. *Tin*, 0.28—1.56%. Resistance to acid is good with small tin content, but diminishes as percentage of tin increases. Atmospheric tests give no particular result. *Tungsten*, 0.40—23.86%. Tests are very good, but irregular. Markedly decreased corrosion is obtained only after high tungsten addition.

There does not seem to be any quantitative relation between acid and atmospheric corrosion.
T. S. P.

Iron and Nitrogen. JOHN H. ANDREW (*J. Iron Steel Inst.*, 1912, 86, 210—235).—A special form of carbon tube electric furnace is used, in which pressures up to 1000 atmospheres may be obtained. Iron is melted in magnesia crucibles, the temperature being determined by means of an optical pyrometer, sighted through a glass window. The iron absorbs small quantities of nitrogen when melted under a high pressure of the gas. The absorption of 0.3% of nitrogen entirely suppresses the critical points of pure iron, and this nitrogen is only removed by prolonged heating in a vacuum. With steel containing 0.6% of carbon, the absorption of 0.25% of nitrogen lowers the A_1 point. Hydrogen has no effect on the critical points of steel when introduced into the liquid metal under pressure.
C. H. D.

The Separation of Graphite in Alloys of Iron and Silicon. GEORGES CHARPY and ANDRÉ CORNU (*Compt. rend.*, 1913, 156, 1616—1618).—In alloys of iron and silicon containing but little carbon, the carbon is entirely precipitated as graphite by annealing, provided that the silicon content is above 3.5% and that the annealing is carried out at a temperature above 750° and below a certain limit temperature, which is a function of the total carbon in the alloy. The bottom limit of this temperature range is lowered and the top limit raised as the percentage of silicon increases, and the top limit is raised when the percentage of carbon increases. W. G.

The Gases Evolved on Heating Steel to its Melting Point in a Vacuum. G. WESLEY AUSTIN (*J. Iron Steel Inst.*, 1912, 86, 236—241).—The iron or steel is used in the form of a cylindrical test-bar, and is enclosed in a gas-tight insulated steel tube and heated by means of an alternating current. The gas is pumped off and analysed. In steels the quantity of gas evolved increases with the carbon content. Cast iron contains a smaller quantity of gas, and the proportion of carbon monoxide is smaller. C. H. D.

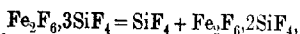
New Method of Revealing Segregation in Steel Ingots. SIR ROBERT HADFIELD (*J. Iron Steel Inst.*, 1912, 86, 40—47).—Segregation in trial ingots of steel may be recognised by adding some molten copper when partial solidification has taken place. The copper remaining liquid longer than the steel is drawn into any cavities which are formed, and is detected by its colour when the solid ingot is cut through.
C. H. D.

The Transformation Points and the Structure of Nickel-chrome Steels. LÉON GUILLET (*Compt. rend.*, 1913, 156, 1774—1776. Compare A., 1903, ii, 650; 1904, ii, 739).—A study of the influence of chromium on the transformation points of nickel steels. The metallographic examination of various alloys shows that for the same content in carbon and chromium a perlitic steel containing nickel possesses a marked tendency for the eutectoid structure; thus a steel containing 0.25% C, 2.40% Ni, and 0.66% Cr has the appearance of an ordinary steel containing 0.75% C, whilst one containing 0.30% C and 0.78% Cr corresponds to an ordinary steel containing 0.35% C. The addition of chromium to a nickel steel acts differently according to the nickel and carbon content of the alloy. Whilst 0.6% Cr does not lower the transformation points of steels containing 2.5 to 3.4% Ni and 0.08 to 0.25% C, an addition of 1.2% Cr produces a marked effect on steels containing 4 to 6.25% Ni, increasing the hysteresis very considerably. W. G.

Ammonium Ferrous Sulphate and its Alkali-metal Isomorphs. ALFRED E. H. TUTTON (*Proc. Roy. Soc.*, 1913, A, 88, 361—387).—A full crystallographic investigation of ammonium ferrous sulphate. The principal conclusion arrived at, which further confirms the deductions from the previous investigations of the zinc and magnesium groups of double sulphates and selenates, and those from the study of the magnesium group of double chromates, is the following: The ammonium salts are truly isomorphous with the potassium, rubidium, and caesium salts of the large monoclinic series of salts having the general formula $R_3M[(S_2Se_2Cr)O_4]_2 \cdot 6H_2O$, but not eutropic with them, the three latter salts alone being eutropic. It is a singular fact that scarcely any change in structural dimensions occurs when ammonium and rubidium are interchanged for each other, that is, when ten atoms ($2NH_4$) replace two atoms (Rb_2), for they do so without appreciably altering the dimensions of the unit cell of the space-lattice.

T. S. P.

The Instability of Ferric Silicofluoride and its Spontaneous Transformation into Another Double Fluoride of Silicon and Iron. ALBERT RECOURA (*Compt. rend.*, 1913, 156, 1618—1620).—In further confirmation of the behaviour of ferric fluoride in solution (compare A., 1912, ii, 353), the author finds that normal ferric silicofluoride cannot exist when it is prepared in solution either by saturating hydrofluosilicic acid with ferric hydroxide, or by double decomposition, since it decomposes immediately according to the equation:



the silicon fluoride liberated being decomposed by the water. On leaving this solution of the ferric silicofluoride to evaporate in the air a colourless syrup is obtained, corresponding in composition with $Fe_3F_6 \cdot 2SiF_4 \cdot Aq$. On pushing the evaporation further in a desiccator, the syrup slowly evolves silicon fluoride, and tends to become transformed into hydrated ferric fluoride.

Chromium silicofluoride undergoes a similar decomposition in aqueous solution. W. G.

Univalent Nickel Compounds. I. ITALO BELLUCCI and R. CORELLI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 603—608).—The present paper deals chiefly with the work of Moore (A., 1894, i, 102; 1895, ii, 168), who by reducing potassium nickelocyanide obtained a red solution, which, he considered, contained a nickel compound of the type Ni_3X_2 . The authors find that Moore's method of analysis (depending on the reduction of ammoniacal silver nitrate) is not sufficiently accurate to support his conclusions. R. V. S.

Chromous Compounds which are Stable in the Air. WILHELM TRAUBE and W. PASSARGE (*Ber.*, 1913, 46, 1505—1508).—The authors have found that chromous salts form stable double compounds with hydrazine or hydrazine salts. They may be exposed to the air for days without changing their properties; in fact, some of them are stable when suspended in water and exposed to the air. Their stability depends probably on their slight solubility in water and also on the reducing properties of the hydrazine; if they are dissolved in acids or in ammonia, the solutions possess the ordinary properties of solutions of chromous salts.

The salts are of the type $\text{MCl}_2 \cdot 2\text{N}_2\text{H}_4$ and $\text{MSO}_4 \cdot (\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4$, where M is a bivalent metal; numerous salts of this type, containing metals other than chromium, are already known (compare Curtius and Schrader, A., 1895, ii, 10; Ferratini, A., 1912, ii, 345).

The general method of preparation is from chromous acetate, which is suspended in air-free water covered with a layer of light petroleum. The acetate is dissolved by the addition of exactly the necessary quantity of dilute acid, and then a solution of hydrazine hydrate or sulphate added. The desired salt precipitates readily, and after being collected it is washed with water, alcohol, and ether and dried over sulphuric acid.

Chromous dihydrazine chloride, $\text{CrCl}_2 \cdot 2\text{N}_2\text{H}_4$, is a lilac-coloured powder, as also is the corresponding *bromide*, $\text{CrBr}_2 \cdot 2\text{N}_2\text{H}_4$. The *iodide*, $\text{CrI}_2 \cdot 2\text{N}_2\text{H}_4$, is greyish-blue. The *double salt* of chromous and hydrazine sulphates, $\text{CrSO}_4 \cdot (\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4$, is a sky-blue, crystalline powder, which is sparingly soluble in water. T. S. P.

A Simple Method for the Preparation of Molybdenum and Tungsten Carbides. SIEGFRIED HILPERT and M. ORNSTEIN (*Ber.*, 1913, 46, 1669—1675).—Molybdenum and tungsten carbides can be obtained by heating the finely powdered metals in carbon monoxide or in a mixture of methane and hydrogen. Experiments made at different temperatures show that the limiting amount of carbon taken up corresponds with simple stoichiometric proportions. These limits, when molybdenum is treated with carbon monoxide, correspond with the carbide, Mo_2C , at 600° and 1000° . At 800° the composition varied between MoC and Mo_2C , the relations being

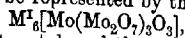
made more complex by the effect of temperature on the equilibrium $2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$, and on the velocity of reaction.

At 1000° tungsten gives the carbide W_2C_4 in carbon monoxide, and the carbide WC in a mixture of methane and hydrogen (1:1) at 800° . The hydrogen is admixed with the methane in order to suppress the dissociation: $\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$.

The carbides are also formed when the trioxides of the metals are used instead of the metals.

T. S. P.

The Constitution of the Paramolybdates and the Paratungstates. HIPPOLYTE COPAUX (*Compt. rend.*, 1913, 156, 1771—1774).—The author suggests that the constitution of the paramolybdates should be represented by the formula



where M^{I} is a univalent metal, and that they are thus derived from an orthomolybdic acid, H_6MoO_6 , by the substitution of Mo_2O_7 for each of three oxygen atoms. Similarly, complex salts, such as sodium molybdoaluminate and molybdoperiodate, would be represented by $\text{Na}_3\text{Al}(\text{Mo}_2\text{O}_7)_3$ and $\text{Na}_5\text{I}(\text{Mo}_2\text{O}_7)_3\text{O}_3$, corresponding with the orthoaluminate, Na_3AlO_3 , and the periodate, Na_5IO_6 .

The paratungstates he considers as hydrotungstates, and represents them by $\text{M}_5^{\text{I}}[\text{H}(\text{W}_2\text{O}_7)_3]$.

In support of these formulae he instances their behaviour with respect to the absorption of ultraviolet light and dehydration on heat; thus the paratungstates absorb less than the metatungstates, but much more than the simple tungstates. Similarly, the paramolybdates absorb less than the silicomolybdates, but more than the simple molybdates or the molybdoperiodates, which are obviously of a complex nature.

W. G.

Crystallisation of Fusions of Tin Chloride with Potassium and Sodium Chlorides. G. RACK (*Centr. Min.*, 1913, 373—379).—Mixtures of tin chloride (m. p. 239°) and potassium chloride (m. p. 777°) in various proportions were fused, and the concentration-temperature diagram given. There are double salts, $3\text{SnCl}_2 \cdot \text{KCl}$ (m. p. 208°) and $\text{SnCl}_2 \cdot \text{KCl}$ (m. p. 224°), and eutectics with 17 mol. % KCl and 38 mol. % KCl at 201° and 180° respectively. The pair tin chloride and sodium chloride (m. p. 800°) yields no double salt, but a eutectic with 32 mol. % NaCl at 183° .

L. J. S.

New Method for the Preparation of Vanadium Tetrachloride. A. T. MERTES (*J. Amer. Chem. Soc.*, 1913, 35, 671—672).—Vanadium tetrachloride can be prepared by passing dry chlorine over ferro-vanadium contained in a hard glass tube and heated by means of a combustion furnace. The reaction takes place thus: $\text{FeV} + 7\text{Cl} = \text{FeCl}_3 + \text{VCl}_4$. The vanadium chloride distils over, whilst the ferric chloride remains in the tube. This method is considered superior to any recorded previously. Vanadium tetrachloride is best preserved by dissolving it in carbon tetrachloride. Ferric chloride is insoluble in this solvent, and hence vanadium chloride can be easily freed from it.

E. G.

The Synthetic Silicates of Bismuth. C. NICOLSCU OTIN (*Bull. Sci. Acad. Roumaine*, 1912-13, 1, 189-196).—Various mixtures of bismuth oxide and silica were melted in an electric furnace, and cooling curves of the fusions taken. The products were also investigated microscopically. Mixtures of bismuth oxide and silica in the following molecular proportions gave rise to compounds: 1:8, 1:3, 1:2, 2:3, 1:1, 3:2, 2:1, 3:1, and 10:1. The respective freezing points (points at which crystallisation commenced), and densities at 20°, of these compounds were as follows: 992°±7°, 6·623; 847°±1°, 8·109; 873°±4°, 8·657; 877-736°, 8·984; 890-772°, 8·924; 791°, 8·388; 803-843°, 9·138; 822°±4°, 8·897; 832°±1°, 9·136. Pure bismuth oxide melted at 825°±1° and had D₂₀ 8·559. T. S. P.

Action of Hypophosphite Solutions on Platinum Salts. ADOLF SIEVERTS [and, in part, ERNST PETERS] (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 263-268).—The paper deals with the investigation of the action of sodium hypophosphite on very dilute solutions of potassium platinochloride. It is shown that the course of the reaction varies with the molecular ratio of the reacting substances. If the hypophosphite is added in great excess ($120\text{NaH}_2\text{PO}_2 : 1\text{K}_2\text{PtCl}_4$), then on warming light brown or yellow stable solutions are formed, which may be evaporated to dryness without decomposition, and do not show the usual platinum reactions. These solutions are shown by ultra-microscopic examination to be solutions of crystalloids. On warming, the yellow solutions give rise to a vigorous evolution of hydrogen, and it is probable that the solution contains a complex compound of platinum chloride and sodium hypophosphite. The smaller the molecular relationship between the reacting substances the darker the solution on warming; if the ratio lies between 20:1 and 40:1 a dark brown solution is obtained, which is not sensitive to the addition of electrolytes, and slowly deposits a precipitate and becomes colourless. This solution also gives a vigorous evolution of hydrogen on warming. Similar dark brown solutions can be obtained by substituting sodium phosphite for the hypophosphite. These solutions liberated hydrogen on warming, but much more slowly than solutions containing hypophosphite. The reddish-brown solutions can be rendered stable by the addition of gelatin or gum arabic, and then show similarities, particularly in respect of their absorption spectra, to the "red platinum" obtained by L. Wöhler (*A.*, 1910, ii, 1075). The evolution of hydrogen is to be represented by the reaction $\text{Na}_2\text{HPO}_3 + \text{H}_2\text{O} = \text{Na}_2\text{HPO}_4 + \text{H}_2$, which is catalysed by the bivalent platinum compound. If the molecular ratio of the reacting substances is made 1:1, then even in extremely dilute solutions greyish-brown to brown liquids are obtained, which are of themselves stable but very sensitive to the addition of electrolytes which produce very rapidly dark-coloured precipitates. These solutions are similar to the black solutions of platinum sols produced by Bredig's method. They act catalytically on hydrogen peroxide and on electrolytic gas at the ordinary temperature with fair rapidity. They are shown by

optical means to be platinum sols of high dispersity. On the addition of an electrolyte the Tyndall cone becomes visible, and particles are visible in the ultra-microscope showing rapid movement. Chloroplatinic acid and potassium platinichloride are not suitable for the preparation of platinum sols, because at an equal dilution they either do not react at all or only very slowly with sodium hypophosphite.

J. F. S.

The Anhydrous Platinum Haloids, PtCl_2 , and PtBr_2 . ALEXANDER GUTBIER and FR. HEINRICH (*Zeitsch. anorg. Chem.*, 1913, **81**, 278—384). [With L. von MÜLLER and J. LIEBERS.]—Anhydrous platonic chloride is most conveniently prepared by heating hydrogen platinichloride in a stream of dry chlorine in an apparatus containing diphenylamine. The product is irregularly crystalline, and not very hygroscopic, but absorbs water slowly.

[With M. BLUMER.]—Platinic bromide has not been obtained in a pure condition. Hydrogen platinibromide is obtained by heating platinum sponge with bromine and concentrated hydrobromic acid in a sealed tube at 180° , but dissociation into platinous bromide and bromine always takes place during drying to an extent which depends on the temperature.

C. H. D.

The Stability Regions of the Four Anhydrous Platinum Chlorides; the Volatility of the Metal in Gaseous Chlorine and the Preparation of Oxygen-free Chlorine. LOTHAR WÖHLER and S. STREICHER (*Ber.*, 1913, **46**, 1591—1597).—The temperatures of decomposition or formation, in an atmosphere of chlorine under normal pressure, were found to be as follows: For platinum tetrachloride, 370° ; at 374° it lost some chlorine, to absorb it again at 364° . The three corresponding temperatures for the trichloride were 435° , 440° , and 430° . The decomposition temperature of platinum dichloride is 582° .

Evidence was obtained for the existence of a yellowish-green platinum monochloride, PtCl , which, however, is stable only over $1\text{--}2^\circ$ between 581° and 583° .

The molecular heats of formation in Calories of the chlorides from chlorine and the next lower chloride are calculated to be: PtCl , 16.10; PtCl_2 , 16.08; PtCl_3 , 13.1; and PtCl_4 , 11.77. The valency isobars of the chlorides of both iridium and platinum do not show any regularities in their relations with each other.

Investigation of the volatility of both iridium and platinum in a current of chlorine showed the formation and volatilisation of exothermic chlorides in the gaseous phase at temperatures above those in which the solid phase could exist.

Oxygen-free chlorine cannot be obtained from potassium permanganate and hydrochloric acid (Wedekind, P., 1909, **25**, 59); it is necessary to use hydrated manganese dioxide in place of the permanganate.

T. S. P.

The Action of Complex-forming Acids or their Salts on Platinum Ammonia Compounds I. Reactions with Potassium Xanthate. LUDWIG RAMBERG (*Ber.*, 1913, **46**, 1696—1700).—Certain acids, especially those containing sulphur, react with

platinum ammonias, ammonium salts being eliminated and salts formed which must be classed as internal complex salts. The reaction takes place according to the scheme: $\text{Pt}(\text{NH}_3)_2\text{X}_2 + 2\text{HA} = \text{PtA}_2 + 2\text{NH}_4\text{X}$, and goes especially readily with the *cis*-platinous ammonias.

By the action of potassium xanthate (2 mols.) on *cis*-dinitratodiammineplatinum, platinous xanthate, $\text{Pt}(\text{S}\cdot\text{CS}\cdot\text{OEt})_2$ (compare A., 1906, i, 791), results, together with considerable quantities of a brown, amorphous powder containing nitrogen. If the ammonia which is eliminated during the reaction is fixed with acetic acid, the yield of platinous xanthate is considerably increased. A similar reaction takes place with *cis*-dichlorodiammineplatinum in the presence of acetic acid; if the molecular proportions used are 1:1, only half the dichloro-compound enters into reaction. When *trans*-dinitratodiammineplatinum is used, an almost quantitative yield of *disanthodiammineplatinum*, $\text{Pt}(\text{NH}_3)_2(\text{S}\cdot\text{CS}\cdot\text{OEt})_2$, is obtained as an almost colourless, microcrystalline powder, which is not soluble in the ordinary solvents without decomposition. The fact that ammonia is not eliminated during the reaction affords fresh support to the idea that ammonia is more firmly bound in the *trans*- than in the *cis*-position. The compound loses ammonia slowly in a desiccator over concentrated sulphuric acid, and all the ammonia is eliminated on solution in glacial acetic acid, giving in this latter case platinous xanthate, two isomeric forms of which do not exist (compare A., 1910, i, 218).

T. S. P.

The Behaviour of Hydrogen towards Palladium. ALEXANDER GUTHRIE, HEINRICH GEBHARDT, and BERTA OTTENSTEIN (*Ber.*, 1913, 46, 1453—1457).—The authors have investigated the absorption of hydrogen by palladium at temperatures varying between -50° and $+105^\circ$. The palladium was used in the form of sponge, which was obtained by heating ammonium palladiochloride in an oxygen-free stream of carbon dioxide, the temperature used being as low as was consistent with the expulsion of all the ammonium chloride. The method of measuring the absorption of hydrogen was similar to that used by Paal and Amberger (A., 1905, ii, 397).

The results obtained are in agreement with those of Paal and Amberger, namely, that with decrease in the temperature there is a considerable increase in the absorption; they contradict the results of Hemptinne (A., 1899, ii, 228) and of Baerwald (*Compt. rend.*, 1907, ii, 202). The absorption is a minimum at 20° .

The palladium hydride obtained was pyrophoric. T. S. P.

The Anhydrous Chlorides of Iridium Corresponding with its Four Stages of Valency. LOTHAR WÖHLER and S. STREICHER (*Ber.*, 1913, 46, 1577—1586).—Anhydrous iridium tetrachloride can be obtained from the trichloride and chlorine only at temperatures under 100° and under high pressures. At 60° and a pressure of less than 20 atmospheres it is formed within five days, using liquid chlorine; at 15° the chlorine pressure is less than 5 atmospheres. The pure substance could not be prepared. The complex H_2IrCl_6

loses hydrogen chloride only at temperatures above 100° , where the pressure of the chlorine is already greater than one atmosphere.

The best method for the preparation of iridium trichloride is by chlorination of the metal at 600 – 620° ; the reaction is complete in a few minutes. Investigation of the chlorine pressure shows that the trichloride can exist under a chlorine pressure of one atmosphere between 763° and $<100^{\circ}$.

The investigation of the chlorine tension of the trichloride led to the discovery of the conditions necessary for the isolation of iridium dichloride, IrCl_2 , and iridium monochloride, IrCl . The former is a brown, crystalline substance which exists between 763° and 773° under a chlorine pressure of one atmosphere; the latter exists under the same conditions between 773° and 798° , and forms copper-red crystals; $D=10.18$. Both the dichloride and monochloride are insoluble in bases or acids, even in concentrated sulphuric acid.

The molecular heats of formation of the mono-, di-, and trichlorides from chlorine and iridium, iridium monochloride and dichloride respectively are calculated to be 20.55, 20.05, and 19.87 Cals. respectively.

T. S. P.

Measurement of the Relative Surface Energy of Iridium Trichloride. LOTHAR WÖHLER and S. STREICHER (*Ber.*, 1913, 46, 1720–1725).—Strongly sintered iridium metal powder, which has been heated to 900° , gives the brown trichloride at 600° (compare preceding abstract). If this is reduced in hydrogen at low temperatures, and again chlorinated at 600° , the yellow trichloride is obtained. On further reduction and chlorination the dark green trichloride results. During these alternating processes the metal produced at the various stages becomes more and more finely divided, that is, more and more rich in surface energy; the same holds for the oxide obtained from the metal. The various trichlorides should therefore owe their colours to the varying stages of fineness of the particles, that is, they should be simply surface modifications; this was shown to be the case by measurements of their absorptive power towards methylene-blue, and of their velocity of sedimentation.

Measurements of their chlorine tension showed that in comparison with the sintered trichloride the surface energy is unexpectedly great, being greater than the difference between the three valency stages of the chlorides.

T. S. P.

Activation of Chlorate Solutions by Osmium. II. KARL A. HOFMANN, OSKAR EHNHART, and OTTO SCHNEIDER (*Ber.*, 1913, 46, 1657–1668).—It has been shown previously (this vol., ii, 62) that feebly acid or neutral solutions of the alkali chlorates readily act as oxidising agents in the presence of traces of osmium tetroxide. Further experiments have shown that the process, in all probability, consists in the formation of an additive compound between the chlorate and the osmium tetroxide, which compound then acts as

the oxidising agent. It cannot be due to the formation of some higher osmium oxide, since osmium tetroxide does not take up oxygen from chlorate solutions, and the lower oxides of osmium take only as much oxygen from the chlorate as to give the tetroxide. Neither is it due to catalytic decomposition of the chlorate, since osmium tetroxide does not appreciably increase the velocity of evolution of oxygen from either solid chlorate or chlorate solutions.

The formation of an additive compound is evidenced by the following: (1) the solubility of potassium chlorate is increased in a solution of osmium tetroxide; (2) the addition of osmium tetroxide to a solution of potassium chlorate raises the oxidation potential to a point which is higher than that of either of the components; (3) the velocity with which iodine is liberated from a solution of potassium iodide indicates that the concentration of the active substance is proportional to the product of the concentrations of the osmium and chlorate.

Chlorate is reduced directly to chloride without the intermediate formation of hypochlorite or chlorite; according to the authors, this is due to the fact that the lower oxide of osmium formed during the process from the additive compound is Os_2O_3 or $\text{OsO}_2, \text{OsO}_3$, and this requires three oxygen atoms for the regeneration of osmium tetroxide.

Comparison of the effects produced by osmium tetroxide and ruthenium hydroxide shows that the former is generally more active; also, owing to the fact that it is soluble in water and therefore has an unlimited surface, it does not show the poisoning phenomena which are generally observed with suspended particles.

Numerous further examples of oxidations brought about by the presence of osmium tetroxide are given. Substances with the ethylene linking, which readily add on halogens or ozone, are attacked, but not so vigorously in a way similar to that in which permanganate acts. The strongly adsorbing, amorphous charcoal is oxidised vigorously, whilst the chemically more active, but weakly adsorbing, amorphous silicon is not acted on. T. S. P.

Mineralogical Chemistry.

Helium in Blue Rock-salt. SIEGFRIED VALENTINER (*Jahrb. Min.*, 1913, i, *Ref.* 195; from *Kali*, 1912, 6, 1—3).—In 1200 grams of the blue rock-salt from Wilhelmshall at Anderbeck was found 1.5 c.c. helium, or 0.13 c.c. per 100 grams, whilst Strutt in 1908 found only 0.0233 c.c. per 100 grams in the ordinary rock-salt from Stassfurt. This much greater amount of helium suggests a radioactive origin for the blue coloration. L. J. S.

Heterolite from Leadville, Colorado. WILLIAM E. FORD and WALTER M. BRADLEY (*Amer. J. Sci.*, 1913, [iv], 35, 600—604).—A dark brown to black mineral with radiating, mamillary structure, found in vugs with hemimorphite and smithsonite at a contact of limestone and quartzite in the Wolfstone mine, is identified with heterolite, a species previously known only from Franklin, New Jersey. The lustre is submetallic, and the streak dark chocolate-brown. Fragments under the microscope are transparent and dark brown, and the fibres are birefringent with straight extinction. $H\ 5\frac{1}{2}$ —6, $D\ 4\cdot6$. The mineral is infusible before the blowpipe; when heated, water, but no oxygen, is expelled. It is easily soluble in hydrochloric acid, with evolution of chlorine. Analysis gave:

ZnO.	MnO.	O.	CaO.	H ₂ O.	SiO ₂ .	Total.	Mn ₂ O ₃ .
37·56	50·34	5·99	trace	4·36	2·69	100·94	56·00

Neglecting silica, these results agree with $4ZnO, 3Mn_2O_3, 2H_2O$. The soluble silica is, however, probably present as admixed hemimorphite, and deducting this, the formula becomes $2ZnO, 2Mn_2O_3, 1H_2O$. Schaller's analysis (A., 1910, ii, 220) of the New Jersey mineral gives the same formula when the water is taken into account.

L. J. S.

The "Hydromagnesite" from Sasbach, Kaiserstuhl, Baden. WILHELM MEIGEN (*Jahrb. Min.*, 1913, i, *Ref.* 202; from *Ber. oberrhein. geol. Ver.*, 1910, 43, 79—80).—The mineral forms hard, nodular, white masses in cavities in lava. Analysis gave: MgO , 47·89; CO_2 , 51·88%, proving it to be pure magnesite. The water shown in earlier determinations is referred to admixed zeolites.

L. J. S.

The So-called Hydrolomite of Marino (Vulcano Laziale). FEDERICO MILLOSEVICH (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 642—647).—Microscopical and chemical examination of this mineral shows that it is not a distinct species, but an aggregate of calcite and hydromagnesite.

R. V. S.

Contact Minerals from the Crystalline Limestones of the Kaiserstuhl, Baden. RICHARD DAUB (*Jahrb. Min.*, 1913, i, *Ref.* 214—217; from *Inaug. Diss. Freiburg i. Br.*, 1912, 45 pp.).—An average sample of 3000 grams of the koppite-bearing limestone from Schelingen was dissolved in dilute acetic acid, leaving a residue of 440 grams, containing: Magnoferrite, 5%; apatite, 5%; koppite, 2%; mica + serpentine, 2·8%; forsterite, 0·2% = 15%. These minerals are each described. The green mica is barytbiotite, and occurs as distinct crystals. It is a mica of the second class, and almost optically uniaxial. The refractive indices (for sodium light, $\gamma = \beta = 1\cdot6053$, $\alpha = 1\cdot5749$) differ but little from those of other biotites, so that barium has little influence on the optical constants. Analysis by M. Dittrich gave 1. Forsterite, $D\ 3\cdot18$ — $3\cdot25$, gave

analysis II by Dittrich, corresponding with $25\text{Mg}_2\text{SiO}_4 + 1(\text{Fe,Mn})_2\text{SiO}_4$:

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	CaO	MgO	BaO	SrO	K ₂ O	Na ₂ O	H ₂ O	Total
I.	29.80	18.43	2.41	0.53	—	8.17	25.02	5.11	trace	5.04	0.29	4.96	99.30
II.	38.74	1.23	1.42	2.25	1.33	1.75	50.54	—	—	0.39	0.16	0.37	98.17

* H₂O below 110°, 0.46; H₂O over 110°, 1.19; H₂O ignition 3.31 = 4.96. TiO₂ nil.

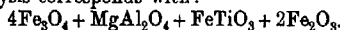
A monticellite-bearing limestone also occurs; this contains also perovskite (dysanallyte) and more rarely diopside, apatite, magnetite, and mica. In a third type of limestone, gehlenite occurs.

L. J. S.

Magnetite from the Kaiserstuhl, Baden. ERNST HUGEL (*Jahrb. Min.*, 1913, i, *Ref.* 200; from *Inaug. Diss. Freiburg i. Br.*, 1912, 47—49).—Indistinct crystals isolated from the crystalline limestone containing dysanallyte, from Vogtsburg, gave:

SiO ₂	TiO ₂	Fe ₂ O ₃	FeO	Al ₂ O ₃	MgO	Total
0.34	4.70	62.39	23.24	6.80	2.59	100.06

Deducting some magnesia and alumina as present in admixed mica, this analysis corresponds with:



L. J. S.

Magnoferite from Kaiserstuhl, Baden. ERNST HUGEL (*Jahrb. Min.*, 1913, i, *Ref.* 200; from *Inaug. Diss. Freiburg i. Br.*, 1912, 50—53).—Analysis of material separated from the limestone of Schelingen gave:

TiO ₂	Fe ₂ O ₃	FeO	Al ₂ O ₃	MgO	MnO	Insol.	Total
1.31	61.95	18.72	6.57	6.74	3.40	1.10	99.79

corresponding with:

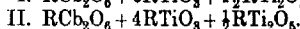
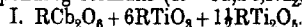


L. J. S.

Dysanallyte from Kaiserstuhl, Baden. ERNST HUGEL (*Jahrb. Min.*, 1913, i, *Ref.* 208—209; from *Inaug. Diss. Freiburg i. Br.*, 1912, 1—46).—Analyses (I, mean of three; II, mean of two) of two samples of dysanallyte from Vogtsburg gave:

	SiO ₂	TiO ₂	CaO	Ce ₂ O ₃	FeO	Al ₂ O ₃	K ₂ O	Na ₂ O	MnO	MgO	Total
I.	0.29	48.31	16.12	21.63	3.32	5.35	1.25	0.39	4.20	0.02	trace
II.	0.33	38.70	25.99	23.51	3.08	5.69	0.82	0.44	1.72	—	—

The corresponding formulæ ($R = \text{Ca, Fe, Na, (CeO)}_2, (\text{AlO})_2$) are:



Uranium is present in traces, and the mineral is slightly radioactive. In one sample, $\text{Ce}_2\text{O}_3 : \text{La}_2\text{O}_3 = 2 : 1$. The large, although variable, amount of columbium indicates that dysanallyte must be regarded as a distinct species (compare O. Hauser, A., 1908, ii, 60).

L. J. S.

Minerals Hitherto Found in the Granulites of Cala Francese on the Island della Maddalena [Sardinia]. DOMENICO LOVISATO (*Mem. R. Accad. Lincei*, 1913, [v], 9, 404—436).—The author enumerates the minerals, thirty-two in number, which he has found in the granulite of this locality in addition to its essential components (quartz, monoclinic and triclinic feldspar and mica biotite). Analyses have been made by Rimatori and by Manis of fourteen of these. R. V. S.

The Melting Point of Silicates. Influence of Size of Grain on Melting Point. Determination of the Melting Point of Some Silicates by Slow Heating. HANS LEITMEIER (*Zeitsch. anorg. Chem.*, 1913, 81, 209—232).—Two specimens of the same mineral, differing only in size of grain, are heated in a platinum boat divided into two compartments, and examined from time to time. The commencement of melting may be affected to the extent of 60—70°, whilst the temperatures of complete liquefaction do not differ more than 20—40°, except in the case of augite.

Finely levigated material is tested in the same manner, heating very slowly, thirty-six to forty-eight hours being taken to reach the melting point. The following results have been obtained, the first temperature in each case being the beginning of melting, the second that of liquefaction: Adularite (St. Gothard), 1145°; augite (Bohemia), 1145—1150°; aegirite (Langesundfjord), 940—950°; labradorite (Kamenybrod), 1245—1250°; diopside (green, from Zillertal), 1260—1290°; diopside (colourless, Rotenkopf in Zillertal), 1295—1320°; diopside (artificial), 1305—1320°. The exact determination of the melting point of natural silicates is almost impracticable, and the meaning of the preliminary sintering is uncertain, although the experiments with adularite suggest that a mineral could be completely melted at the sintering temperature if sufficient time were allowed. C. H. D.

Melting Phenomena of the Plagioclase Feldspars. N. L. BOWEN (*Amer. J. Sci.*, 1913, [iv], 35, 577—599).—The following determinations of the melting intervals were made by the method of quenching. A charge, after being kept at a definite temperature for one hour, was suddenly chilled in mercury, and the material then examined under the microscope for the presence of glass or crystals. The pure artificially prepared materials previously examined by Day

Composition.	Temp. of beginning of melting.	Temp. of completion of melting.
	Solidus.	Liquidus.
An	1550° ± 2°	1550° ± 2°
Ab ₁ An ₉	1465 ± 4	1521 ± 2
Ab ₁ An ₉	1372 ± 4	1490 ± 2
Ab ₁ An ₁	1287 ± 4	1450 ± 2
Ab ₁ An ₁	1205 ± 5	1394 ± 2
Ab ₁ An ₁	1175 ± 8	1362 ± 2
Ab ₁₇ An ₈₃	1158 ± 5	—
Ab ₁ An ₁	—	1334 ± 2
Ab ₃ An ₁	—	1265 ± 3
Ab ₃ An ₂	1100 ± 10	—

and Allen (A., 1906, ii, 177) were used. Mixtures richer in albite than Ab_2An_1 could not be completely crystallised, and were therefore of no use for fixing the solidus point; in this case the natural crystallised feldspars were employed—oligoclase, $\text{Ab}_{77.5}\text{An}_{22.5}$, from Bakersville, North Carolina, and albite, $\text{Ab}_{98}\text{An}_2$, from Amelia Co., Virginia.

These results are plotted on a temperature-concentration diagram, and are confirmed by determining the composition of the liquid phase (the quenched glass) by means of the refractive indices. This diagram demonstrates the great difference in composition of the liquid and solid phases at any temperature, and explains why the composition of the crystals (zoned crystals in igneous rocks) continuously changes with falling temperature, becoming progressively more acid. From theoretical considerations on the lines suggested by van Laar (A., 1906, ii, 422), the latent heats of melting are calculated as 104.2 cal. per gram for anorthite, and 48.5 for albite.

L. J. S.

Talc of "Grangie Subiaschi" in Val Pellice (Alpi Cozie) and the Minerals Associated with it. ALESSANDRO ROCCATI (*Atti R. Accad. Sci. Torino*, 1912-13, 48, 630-642).—In this locality three varieties of talc can be distinguished: (1) a compact, white substance without included minerals, giving on analysis numbers pointing to the formula $\text{H}_2\text{Mg}_3\text{Si}_4\text{O}_{12}$; (2) a greenish-white, laminated talc of the formula $\text{H}_4\text{Mg}_6\text{Si}_7\text{O}_{22}$; (3) minute laminae of talc in a calcareous matrix; this variety has a composition corresponding with the formula $\text{H}_4\text{Mg}_3\text{Si}_6\text{O}_{19}$. The associated minerals include an actinolite, sp. gr. 3.01, having a composition corresponding with the formula $3(\text{Mg},\text{Fe})\text{SiO}_3, \text{CaSiO}_3$, pyrites, limonite, and a garnet having a composition required by the formula $3\text{CaO}, (\text{Al},\text{Fe})_2\text{O}_3, 3\text{SiO}_2$. Nodules (sometimes of large size), consisting chiefly of hyaline quartz, are also found included in the talc.

R. V. S.

The Acidulo-alkaline Water of Uliveto. New Analyses and Physico-chemical Researches. RAFFAELE NASINI, LUIGI MARINO, FERNANDO AGENO and C. PORLEZZA (*Gazzetta*, 1913, 43, i, 321-353).—This paper gives a detailed account of the composition and properties of this water. The gases dissolved in 1 litre at 27.6° comprise carbon dioxide, 769.12 c.c.; oxygen, 0.33 c.c.; nitrogen and rare gases, 16.81 c.c. The total solids of 1 litre of the water amount to 2.4400 grams (dried at 105°) or 2.3800 grams (dried at 180°). The composition of the residue (expressed as metallic and acid radicles) is Na 0.35331, Li 0.00066, Ca 0.43436, Mg 0.03900, Cl 0.36075, SO_4 0.44868, CO_3 0.62475, $(\text{P}_2\text{O}_5, \text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3)$ 0.00466, SiO_2 0.02036; total, 2.28653. The waters are notably radioactive, the activity being chiefly due to radium emanation. The gas obtainable from the water contains much helium.

R. V. S.

Analytical Chemistry.

A Compact, Accurate Burette for Use in Nitrogen Work or Whenever Many Measurements of Standard are Necessary.

FRANK C. GEPHART (*J. Ind. Eng. Chem.*, 1913, 5, 490).—The burette consists of three bulbs of such capacity that the marks on the narrow portion of the burette beneath them read, respectively, 25, 15, and 10 c.c., reading from the top. It is connected to the stock of standard solution by a side-tube opening beneath the lowest graduation.

T. S. P.

Extraction Apparatus. WALTHER FRIESE (*Pharm. Zentr.-h.*, 1913, 54, 541—542).—The substance to be extracted is placed in a cylindrical vessel supported in a wider tube; the top of the latter is connected with a reflux apparatus, whilst its lower end is contracted so as to form a tube which passes through the cork of the extraction flask. The solvent falls from the condenser into a small funnel tube which reaches to the bottom of the cylindrical vessel; the solvent continuously rises in the latter, flows over the upper edge, and returns to the extraction flask.

W. P. S.

Juice of the Blueberry as an Indicator. G. N. WATSON (*Amer. J. Pharm.*, 1913, 85, 246—247).—Blueberry juice when carefully neutralised imparts an olive-green colour to alkaline and a rose colour to acid solutions. The author states it may be used in volumetric analysis instead of cochineal or litmus. Like the latter, it is sensitive to carbon dioxide, which, if present, should therefore be removed by boiling.

L. DE K.

An Electric Desiccator for the Analysis of India Rubber and Other Organic Compounds. L. J. D. HEALY (*J. Ind. Eng. Chem.*, 1913, 5, 489—490).—The desiccator possesses a side-tube connecting with a manometer and vacuum pump, and also an opening in the top, through which passes a thermometer. A resistance is inside the desiccator, and is connected with a lamp rheostat, so arranged that any temperature from 45—175° can be obtained. The procedure in drying rubber is as follows: After being placed in the desiccator the latter is exhausted and heated to about 60°, the current being left on for an hour. If the pressure at any time rises to more than 75 mm. the desiccator is again exhausted. At the end of the hour the desiccator is allowed to cool and air admitted. This procedure is repeated until the weight of the rubber is constant. The process takes four to five hours as compared with about two hundred hours by the ordinary method.

T. S. P.

Assay of Bleaching-powder or Hypochlorites. F. DUCCELLIEZ (*Bull. Soc. chim.*, 1913, [iv], 13, 494—497).—The method proposed by Hanriot and subsequently investigated by Blattner for the assay of

bleaching agents yielding chlorine has been re-examined. The method depends on the measurement of the oxygen liberated when nickel or cobalt oxide is placed in contact with a hypochlorite. The liberation of oxygen is very slow at 20°, but becomes rapid at 45°. The author suggests the use of cobalt chloride in presence of alkali as a catalyst, and describes an apparatus for carrying out the estimation. The results quoted indicate that the process is rapid and accurate.

T. A. H.

Colour Reactions of Chlorates. M. EMMANUEL POZZI-ESCOFFIER (*Bull. Soc. chim.*, 1913, [iv], 13, 498—499).—In connexion with the colour reaction for chlorates described by Pieraerts (this vol., ii, 238) the author points out that the sensibility is greatly increased by using sulphuric acid in place of hydrochloric acid, and that the substitution of benzidine for aniline results in the production of an orange-yellow coloration, which forms a still more sensitive test. Further, in presence of sulphuric acid aniline gives a blue coloration with chlorates and reddish-brown with nitrates or iodates. Benzidine, however, gives the same coloration with all three kinds of salts. Directions for applying the test are given.

T. A. H.

Fluorine in Reagents. P. CARLES (*Bull. Soc. chim.*, 1913, [iv], 13, 553—556).—Methods of detecting fluorine in, and of eliminating it from, a number of common reagents are described. Sulphuric and hydrochloric acids are usually free from fluorine, but nitric acid almost always contains it, as does also potassium nitrate. Barium hydroxide of commerce always contains insoluble fluorides, so that clear solutions are generally free from fluorine, and this is also the case with barium acetate. Sodium hydrogen carbonate and the corresponding potassium salt are rarely free from fluorine, and ammonium carbonate always contains it. Crystallised acetic acid carefully freed from the mother liquor is free from fluorine.

T. A. H.

Use of Sodium Potassium Tartrate in the Estimation of Oxygen in Water. J. J. VAN ECK (*Chem. Weekblad*, 1913, 10, 455—464).—A summary of previous work on the use of sodium potassium tartrate in the estimation of oxygen in water, and a discussion of the cause of the low values obtained with certain types of salt solution, and of the lack of definiteness in the end-point of the reaction.

A. J. W.

Estimation of Sulphur in Illuminating Gas. R. S. McBRIDE and E. R. WEAVER (*J. Ind. Eng. Chem.*, 1913, 5, 474—476).—A comparison of the referee's, Hinman-Jenkins, and Elliott apparatus for the estimation of sulphur in gas showed that any one of these apparatus is capable of giving satisfactory results when due precautions are taken.

The referee's apparatus is the ordinary one used in such tests. The Elliott apparatus is essentially the same, the principal difference being the use of two condensing cylinders through which the

gases pass successively. The Hinman-Jenkins apparatus differs from the referee's greatly in form, but in principle only in the use of concentrated ammonium hydroxide instead of ammonium carbonate as a source of ammonia.

T. S. P.

Rapid Estimation of Sulphur in Pyrites Cinder. A. B. CONNER (*J. Ind. Eng. Chem.*, 1913, 5, 399—401).—The method described by Nitchie (A., 1912, ii, 682) was found to be trustworthy. W. P. S.

Apparatus for the Precipitation of Barium Sulphate under Varying Conditions. H. G. SMITH (*J. Ind. Eng. Chem.*, 1913, 5, 416—417).—The solution containing the sulphate is heated to boiling in a beaker, and a bent test-tube containing barium chloride is placed in the beaker during this period. The test-tube has a capillary opening in its side near the upper end, and when the solution boils, the test-tube is placed across the top of the beaker so that the hot barium chloride solution flows slowly through the capillary into the solution in the beaker.

W. F. S.

Estimation of Sulphate in Ammonium Sulphate Solution, with Special Reference to the Testing of Illuminating Gas. R. S. McBAIRD and E. R. WEAVER (*J. Ind. Eng. Chem.*, 1913, 5, 469—474).—The authors have tested the various methods for the estimation of sulphate in solutions such as are obtained in the estimation of sulphur in coal gas, that is, which may contain ammonium carbonate and silica (dissolved from the glass). For ordinary purposes an accuracy of 2—3% is ample.

For accurate work the gravimetric methods, using the precautions usually taken, are to be preferred. For rapid work the volumetric and nephelometric methods are useful. The volumetric method tested was very similar to that of Holliger (A., 1910, ii, 239), and is as follows: 300 c.c. of the sample are acidified with 10 c.c. of hydrochloric acid (1:1). the solution is heated to boiling, and then 15 c.c. of barium chloride solution (50 grams per litre) added. After boiling for five minutes 15 c.c. of potassium dichromate solution (30.5 grams per litre) and a few drops of a dilute solution of ferric chloride are added, after which precipitation is brought about by excess of ammonium hydroxide. After boiling for five minutes, the precipitate is collected, well washed, and the chromate in the filtrate estimated iodometrically. A blank estimation is necessary.

In the turbidimetric method the neutralised solution of the sulphate is precipitated at 25—30° with barium chloride, and the turbid liquid poured into a graduated glass cylinder until the filament of an electric lamp placed below just cannot be seen. By comparison with results obtained with solutions of known strength, the percentage of sulphate can then be estimated.

T. S. P.

Estimation of Polythionate in Presence of Thiosulphate and Free Sulphur Dioxide. WALTHER FELD (*Zeitsch. angew. Chem.*, 1913, 26, 286—288).—The process is as follows: The sulphur

dioxide and thiosulphate are titrated with iodine. The resulting free acid is titrated with sodium hydroxide after adding ammonium chloride and methyl orange. Half of the alkali consumed equals the iodine taken up by sulphur dioxide; the remaining iodine represents the thiosulphate. Another part of the solution is now shaken for half an hour with an emulsion of manganous sulphide, made up to a definite bulk and filtered. An aliquot part of the filtrate is boiled with excess of mercuric chloride solution, ammonium chloride is added, and the acidity liberated is titrated with sodium hydroxide and methyl-orange. The acidity which represents the sulphur dioxide and thiosulphate is deducted from the total acid; the balance represents the S_2O_4 (polythionate).

The emulsion is prepared as follows: 600 c.c. of a normal solution of manganous sulphate are heated to 60° , and a rapid stream of hydrogen sulphide is passed; a few drops of aqueous potassium hydroxide are added, and the liquid is filtered. After again heating at 60° a rapid stream of the gas is passed while adding drop by drop a solution of potassium hydroxide (about 50 grams) so as to precipitate about 80–85% of the manganese present. After expelling the excess of hydrogen sulphide by heating in a water-bath at 80° , the mixture is ready for use.

L. DE K.

Estimation of Ammonia by the Formaldehyde Method and of Formaldehyde by means of Ammonia. M. EMMANUEL POZZI-ESCOR (*Ann. Chim. anal.*, 1913, 18, 193–194).—The author points out that the formaldehyde method described by Gaillot (this vol., ii, 240) for the estimation of ammonia is not new, and that it is, moreover, less trustworthy than the ordinary distillation method. The converse reaction may, however, be used for the estimation of formaldehyde if the influence of the ammonium salts is taken into consideration (compare A., 1908, ii, 320).

W. P. S.

The Application of Folin's Method for the Estimation of Ammonia to Fertilisers. OTTO FOLIN and ALFRED W. BOSWORTH (*J. Ind. Eng. Chem.*, 1913, 5, 485).—Two grams of the fertiliser are placed in a 100 c.c. graduated flask, about 50 c.c. of water added, and then 25 c.c. of approximately normal hydrochloric acid. After making up to 100 c.c. the contents of the flask are well shaken, and again after a few minutes. When the heaviest undissolved particles have settled, 5 c.c. of the supernatant liquid are transferred to the tube of the Folin apparatus (compare A., 1903, ii, 239), and the ammonia estimated according to Folin's method (compare Folin and Farmer, A., 1912, ii, 702).

T. S. P.

Estimation of Hydroxylamine. ERWIN RUPP and H. MADER (*Arch. Pharm.*, 1913, 251, 295–300).—Meyeringh's method for the estimation of hydroxylamine, which involves oxidation by iodine in presence of magnesia or sodium phosphate and titration of the excess of iodine, is shown to be subject to two errors: (1) that the sodium phosphate or magnesia used may convert some of the iodine into iodide or hypiodite, and (2) that the nitrous oxide formed may be in part oxidised by the iodine, and thus use up some of

the reagent. Actual trials showed that very different quantities of iodine are needed, depending (a) on the nature and quantity of the material employed to absorb the hydriodic acid formed in the reaction, and (b) on the time during which the reaction mixture is allowed to stand.

Titration by means of sodium hypobromite is suggested. Ten grams of sodium hydroxide are dissolved in water, 15 grams of bromine added, and the solution made up to 1000 c.c. The strength of this solution is then determined by diluting 20 c.c. with 50 c.c. of water, adding 1 gram of potassium iodide and 20 c.c. of dilute hydrochloric acid, and titrating with *N*/10-sodium thiosulphate. For estimating hydroxylamine, 20 c.c. of the sodium hypobromite solution is mixed with 75 c.c. of water, and hydrochloric acid added drop by drop until the colour changes from yellow to the brown of bromine. Not more than 0.01 gram of hydroxylamine is then added, and the mixture, after standing five minutes, titrated with sodium thiosulphate solution, after the addition of potassium iodide and hydrochloric acid.

T. A. H.

Gas Analytical Estimation of Nitric Oxide and Oxygen, Depending on the Smooth Formation of Nitrous Acid Anhydride from these Gases. GABRIEL KLINGER (*Ber.*, 1913, 46, 1744—1748).—The method for the estimation of nitric oxide has been given previously (this vol., ii, 74); that for oxygen is simply the reverse, and follows as a matter of course. It should be noted especially that the gases and stick potassium hydroxide used must be dry, otherwise nitrous acid is formed, which is oxidised by the excess of nitrogen trioxide to nitric acid.

The nitric oxide used should be dried by passing it through concentrated sulphuric acid. Mercury is used as the liquid in the burette and potassium hydroxide pipette.

T. S. P.

Effect of Sulphates on the Estimation of Nitrates. WALTER P. KELLEY (*J. Amer. Chem. Soc.*, 1913, 35, 775—779).—In connexion with a study of the estimation of nitrates in soil extracts by the phenoldisulphonic acid method, Lipman and Sharp (*Univ. Cal. Publ. in Agric. Sci.*, 1912, 1, 21) have stated that on evaporating a nitrate solution containing sodium sulphate considerable loss of nitrate takes place.

It has now been found that in presence of the sulphate of sodium, potassium, or ammonium, loss of nitrate occurs, but that the sulphates of calcium and magnesium do not occasion any loss. It is shown that the loss is due to the presence of small quantities of the hydrogen sulphate, either contained in the sulphate or produced by slight hydrolysis. If sodium carbonate is added to the solution before evaporation, the loss is entirely prevented.

E. G.

Detection of White Phosphorus in Matches, etc. F. SCHRÖDER (*Arch. K. Gesundheit*, 1913, 44. Reprint, 29 pp.).—The material is treated with a little benzene, and a strip of filter paper 10 cm. long

and 3 cm. in diameter is soaked in it. This is then suspended in a glass tube connected to a Victor Meyer's heating apparatus, and exposed to a current of air at 40–50°. Even when the benzene solution contains no more than 0.01 milligram of white phosphorus per c.c. the paper will soon become luminescent. The test must, of course, be carried out in a perfectly dark room. Other varieties of phosphorus do not give the reaction.

L. DE K.

Estimation of Phosphorus in Steels Containing Vanadium. JOHN R. CAIN and F. H. TUTTLE (*J. Washington Acad. Sci.*, 1913, 3, [9], 249).—In order to ensure a complete precipitation of the phosphorus in presence of vanadium by the molybdate process and the formation of a pure "yellow precipitate," a slight excess of ferrous sulphate should be added, and the following conditions should be observed: The precipitation should take place at 15–20°, so as to prevent rapid oxidising action on the vanadium or the ferrous sulphate by the nitric acid; the partial neutralisation with ammonia must be made before adding the iron sulphate; otherwise the liquid might get too warm. If oxides of nitrogen are formed, these interfere with the complete precipitation of the phosphorus owing to re-oxidation of the vanadyl salt. A good shaking apparatus should be used.

L. DE K.

Volumetric Estimation of Hypophosphorous Acid and Hypophosphites. LUIGI MARINO and A. PELLEGRINI (*Gazzetta*, 1913, 43, i, 494–497).—The methods which have been proposed for titrating hypophosphite solutions are not entirely satisfactory. Rapid and accurate estimation is, however, possible, if the oxidation of the hypophosphorous acid is effected by the $N/5$ -alkaline permanganate prepared as described for the estimation of selenious acid (Marino, A., 1910, ii, 155). The alkaline permanganate is added to the dilute hypophosphite solution until a permanent pink coloration is obtained; the liquid is then acidified with sulphuric acid, and the excess of permanganate is titrated in the usual way.

R. V. S.

Estimation of Phosphoric Acid. LUDWIG MOESER and G. FRANK (*Zeitsch. anal. Chem.*, 1913, 52, 346–349).—About 0.5 gram of native phosphate is heated to boiling with 4–6 c.c. of strong sulphuric acid in a round-bottomed flask for ten to fifty minutes; care must be taken that the mass shall not get dry. When cold the mass is extracted with 30–40 c.c. of 95% alcohol, which completely dissolves the phosphoric acid. In order to render the solution more filterable, 2 c.c. of 10% alcoholic potassium hydroxide are added, which causes a precipitate of potassium sulphate.

From the filtrate (after diluting this with an equal volume of water) the phosphoric acid is precipitated by adding slight excess of ammonia, and then, after heating to boiling, magnesium mixture.

Manganese, if present in more than traces, interferes with the process. In such cases a precipitation of the phosphoric acid as the ammonium manganese compound is proposed.

L. DE K.

Estimation of Water-soluble Phosphoric Acid in Ammonium Superphosphates. (Influence of Temperature.) ERNST BÜTNER (*Chem. Zeit.*, 1913, 37, 662).—The author finds that about 0.5% more water-soluble phosphoric acid is found when ammonium superphosphate is shaken for thirty minutes with water at a temperature of 18–20° than when the temperature is allowed to fall to 16° during the shaking operation. The solubility of the phosphate also increases with the fineness of the superphosphate. W. P. S.

Preparation of Petermann's Solution. F. ZÖHREN (*Chem. Zeit.*, 1913, 37, 611–612).—To prevent loss of ammonia during the preparation of Petermann's solution for the estimation of citrate soluble phosphoric acid, it is recommended that the citric acid solution be placed in a flask provided with a side-tube connected with a small flask containing a portion of the citric acid solution. The larger flask is closed with a rubber stopper, and the ammonia is added gradually through a tube passing through the stopper and extending beneath the surface of the solution in the flask; the latter is provided with a stirring apparatus, and may be cooled during the addition of the ammonia. When all the ammonia has been introduced, the contents of the smaller flask are added.

W. P. S.

Effect of Ignition on the Solubility of Soil Phosphates. GEORGE S. FRAPS (*J. Ind. Eng. Chem.*, 1913, 5, 416).—When soil is ignited the quantity of phosphoric acid soluble in dilute hydrochloric acid is increased, although it may, or may not, be rendered more soluble in hot nitric acid. It may be concluded that a portion of the phosphoric acid, rendered soluble by ignition, is probably of inorganic origin.

W. P. S.

Estimation of Active Oxygen in Perborates and in Washing Powders Containing the Same. FRANZ M. LITTELSCHIED and P. B. GUGGIARI (*Chem. Zeit.*, 1913, 37, 690–691).—The available oxygen in perborates may be conveniently found from the loss in weight when 2 grams of the sample are treated with dilute (25%) sulphuric acid and about 2 grams of purified manganese dioxide in a Geissler carbon dioxide apparatus. One-half of the loss in weight = available oxygen.

In applying the process to washing mediums, 20 grams of the sample are treated with 120 c.c. of water at 70°; dilute (25%) sulphuric acid is slowly added to expel carbon dioxide, and the whole is made up to 200 c.c. One gram of kieselguhr is added, and the mixture well shaken and filtered. An aliquot part of the solution is then tested as described in the Geissler apparatus.

L. DE K.

New Rapid Method for the Estimation of Carbon in Iron and its Alloys. ERNST SZÁSZ (*Zeitsch. angew. Chem.*, 1913, 26, 281–284).—A rather complicated apparatus is described and

figured for the combustion of iron and its alloys in a small volume of absolutely pure oxygen; the resulting carbon dioxide is then measured in the usual manner in a gas burette; it may also be collected in a weighed absorption apparatus.

The combustion of alloys liable to cake should be carried out with addition of alumina; for ferromolybdenum, addition of heavy magnesium oxide is recommended so as to prevent volatilisation of molybdenum trioxide, which otherwise might cause an obstruction.

L. DE K.

A Vitrified Clay Combustion Tube with Tapered Outlet for the Estimation of Carbon in Steels, Ferro-alloys, and Graphite. CHARLES MORRIS JOHNSON (*J. Ind. Eng. Chem.*, 1913, 5, 488).—The author has found a vitrified clay combustion tube to be a more than satisfactory substitute for a silica tube, since it is not so readily affected by basic material.

T. S. P.

Estimation of Total Carbon in Soils. M. EMMANUEL POZZI-ESCOR (*Bull. Assoc. chim. Sucr. Dist.*, 1913, 30, 618—621).—A quantity of the soil, containing not more than 0.3 gram of organic matter, is mixed in a nickel boat with 0.1 gram of fused potassium dichromate and 1 gram of lead chromate, and the combustion is then carried out in the usual way. A large excess of oxygen must be employed, but the rate at which this gas is passed through the combustion tube must be slow. The tube should be packed with copper oxide (in the form of threads) for a length of at least 350 mm., and the usual piece of copper foil may be replaced by silvered pumice. The carbon dioxide formed is absorbed in a suitable apparatus and weighed. The author criticises a method described recently by Grégoire (this vol., ii, 243), in which a large quantity of soil is heated with a relatively small quantity of copper oxide, and the resulting carbon dioxide absorbed in barium hydroxide solution, the latter being then decomposed and the volume of the liberated gas measured.

W. P. S.

Gravimetric Estimation of Carbon Dioxide. A. DEJEANNE (*Bull. Soc. chim.*, 1913, [iv], 13, 556—560*).—The method depends on the absorption of the carbon dioxide in an excess of a standard solution of barium, calcium, or strontium hydroxide. To this liquid, which now contains the carbonate in suspension, a known quantity of magnesium chloride is added. In these conditions the magnesium hydroxide formed is precipitated completely, carrying the carbonate (in suspension) with it. The quantity of barium, calcium, or strontium in an aliquot part of the clear mother liquor is then estimated as the sulphate, oxalate, or carbonate respectively.

T. A. H.

The "Application" of [the] Fontactoscope in the Estimation of the Emanation Content of Spring Waters. W. HAMMER and FR. VOHSEN (*Physikal. Zeitsch.*, 1913, 14, 451—454).—When radioactive water is shaken with air in a closed fontactoscope, and

* and *Ann. Palsif.*, 1913, 6, 335—339.

the saturation current measured after different intervals of time, it is found that in the early stages the decay curve which is obtained deviates considerably from the theoretical curve. This has been found to be due to the liberation of the solid disintegration products in the process of shaking. The fine spray containing the dissolved solids settles after a time, and the later portion of the decay curve agrees with that obtained for pure radium emanation.

For exact measurements, it is recommended that observations should not be made until three hours have elapsed since the active water was shaken up with the air enclosed in the apparatus. The disturbance is, however, quite small at the end of fifteen minutes, and for many purposes observations may be commenced after this shorter time interval.

H. M. D.

Estimation of the Soluble Salts in Soils by Electric Methods. A. FLODERER-MAGYARÓYAR (*Bied. Zentr.*, 1913, 42, 228—230; from *Mitt. deut. landw. Ges.*, 42, 579).—In estimating the soluble salts in soils it is necessary to take into account the amount of moisture in the soil, the temperature, the specific conductivity of the salts in different concentrations, and the structure of the soil.

N. H. J. M.

Control of the Purification of Boiler Feed-Water. C. BLACHER (*Zeitsch. angew. Chem.*, 1913, 26, 288).—A reply to Weissenberger (this vol., ii, 338). The author states that his improved dropping flasks are correct to 0.25 German degree.

L. DE K.

Differentiation of the Magnesium Hardness in Water, Especially with Regard to the Hardening of River Water by the Waste Liquors from Potassium Chloride Factories. HERMANN NOLL (*Zeitsch. angew. Chem.*, 1913, 26, 320—327).—The author gives further details of his method of differentiation of the magnesium hardness into carbonate and non-carbonate hardness (compare A., 1912, ii, 997). He has also investigated the applicability of Precht's method (A., 1879, 1053) of determining the magnesium chloride content of potassium salts to the investigation of waters. For this purpose a known volume of water is evaporated to dryness, the residue dried at 110° during half an hour, cooled and extracted with 96% alcohol, the magnesium chloride being determined gravimetrically in the extract. This method differs from that devised by the author, in that only the magnesium chloride is determined in the former, whilst the total non-carbonate hardness due to magnesium salts is estimated in the latter.

The author is led to the conclusion that neither method yields strictly accurate results, but that the figures obtained by his own method are the more closely in accord with the actual state of equilibrium of the dissolved salts. Determinations of alkalinity and magnesia in the concentrated water readily give results which are of comparative value, whilst a combination of the two methods allows an approximate differentiation of the non-carbonate hardness due to magnesia.

H. W.

The Presence of Strontium Compounds in Blende. EDGAR BEYNE (*Bull. Soc. chim. Belg.*, 1913, 27, 159—164).—The author finds that zinc blende may contain strontium in quantities up to 4.8% (expressed as SrO), the strontium being present probably in the form of carbonate. In the ordinary course of analysis the strontium would be precipitated with the barium and included with this in the final statement, thus introducing the possibility of a considerable error in the calculation of the sulphur which should not be removable by roasting. It is suggested that the mixed precipitate of barium and strontium sulphates should be treated with fusion mixture, and the barium precipitated from the acetic acid solution as chromate, then reprecipitated and weighed as sulphate; the strontium in the filtrate and washings is then collected as carbonate, being afterwards also reprecipitated and weighed as sulphate.

D. F. T.

Spelter Analysis. ERIC J. ERICSON (*J. Ind. Eng. Chem.*, 1913, 5, 401—402).—Methods are described for the estimation of lead, iron, and cadmium; copper, tin, and antimony may also be separated when present in the spelter, and the amount of zinc is found by difference. The sample is treated with dilute hydrochloric acid for fifteen hours, and the insoluble portion separated by filtration: this insoluble portion is then dissolved in nitric acid, tin and antimony oxides are removed, and the lead is estimated in the filtrate by the volumetric method described previously by the author (A., 1904, ii, 780). Cadmium is estimated in the ammoniacal filtrate from the lead dioxide, by double precipitation as sulphide, trichloroacetic acid being employed in separating traces of zinc in the second precipitation (T., 1907, 91, 964). Iron is estimated in another portion of the sample by titration with permanganate.

W. P. S.

Rapid Technical Estimation of Lead Dioxide in Red Leads. CESARE FINZI and ERNESTO RAPUZZI (*Zeitsch. anal. Chem.*, 1913, 52, 358—367).—The apparatus consists of a 200—250 c.c. flask fitted with a doubly perforated cork, through which pass a stop-cock funnel and an exit tube, which is connected by means of a rubber tube (fitted with a pinch-cock) with a nitrometer. Fully 1 gram of the sample is introduced into the flask, also 30—40 c.c. of water, and the air is expelled by boiling; a little more water is introduced through the funnel, and the boiling continued for a while. The rubber tube is then temporarily closed with the pinch-cock, and the flame again removed. When cooled somewhat, 20 c.c. of hydrazine reagent are introduced, a slight heat is applied, and the nitrogen evolved is collected and measured with the ordinary precautions. One atom of nitrogen = 1 mol. of lead dioxide. The reagent is prepared as follows. Sufficient hydrazine sulphate to yield a 12% solution of hydrazine acetate is decomposed by means of barium acetate. The liquid is filtered, and 10% of acetic acid added.

L. DE K.

Some Sensitive Copper Reactions. Detection of Copper by means of Dextrose. DANIEL SCHENK (*Chem. Zentr.*, 1913, i, 1233; from *Apoth.-Zeit.*, 1913, 28, 137).—The reversed Fehling's reaction will detect 1/20,000 gram-mol. crystallised copper sulphate in a litre.
J. C. W.

The Analysis of Copper Tin Alloys. WILLIAM GEMMELL (*J. Soc. Chem. Ind.*, 1913, 32, 581—584).—In the estimation of tin in a copper tin alloy by treating with nitric acid, and obtaining the tin directly as stannic oxide, the last-named substance is always yellow, due to the presence of copper and iron oxides. To avoid this source of error, the author dissolves two grams of the alloy in a mixture of 10 c.c. of nitric acid (D 1.42) with 10 c.c. of sulphuric acid (D 1.84) and 30 c.c. of distilled water; both copper and tin dissolve completely, and after expelling oxides of nitrogen and diluting with an equal bulk of water, the copper is estimated by deposition on a rotating platinum electrode. The tin in the remaining solution can be precipitated as stannic oxide by diluting and boiling, or more conveniently by pouring into a cold 2% solution of sulphuric acid saturated with hydrogen sulphide; it is then dissolved in ammonium sulphide and the tin estimated electrolytically.

For the estimation of lead 5—10 grams of the alloy are dissolved in the above acid mixture, and the solution evaporated until the sulphuric acid fumes; the liquid is then diluted, and the lead sulphate collected and weighed. Iron, nickel, and zinc can be successively estimated in the usual manner in the solution from which copper and tin have been removed; the iron is precipitated with ammonium hydroxide, the nickel with dimethylglyoxime, and the zinc then calculated by difference or estimated electrolytically; as an alternative the iron and nickel can be precipitated together by sodium hydroxide and separated afterwards.
D. F. T.

Analysis of a Mixture of Sodium Carbonate and Copper Sulphate. HENRI J. F. DE VRIES (*Zeitsch. anal. Chem.*, 1913, 52, 350—357).—Two grams of the mixture (an insecticide used in agriculture) are dissolved in a known volume of *N*/5-sulphuric acid, the carbon dioxide is boiled off, and the liquid, when cold, diluted to 100 c.c. Of the filtrate, 25 c.c. are now titrated with *N*/10-sodium hydroxide, the end-point being shown by a slight separation of basic copper sulphate. This gives the sodium carbonate. Solution of phenolphthalein is now added, and the titration continued with continuous shaking until the colour of the precipitate formed turns ultramarine or violet-blue. This gives the copper sulphate. The relation between the alkali and copper sulphate must be determined by a practical experiment. The analysis should be controlled by a determination of the carbon dioxide, say, by means of Scheibler's apparatus. If this, calculated to sodium carbonate, should exceed the titration result, sodium hydrogen carbonate is present, which may be found by an easy calculation and then allowed for.
L. DE K.

Estimation of Manganese in Soils. MILAN J. STRITA (*Zeitsch. anal. Chem.*, 1913, 52, 337—345).—The process is intended for soils moderately rich in calcium. Fifty c.c. of a 25% hydrochloric acid extract (=10 grams of sample) are evaporated in a 200 c.c. flask, with addition of 25 c.c. of fuming nitric acid, to a small bulk, and then further evaporated in a porcelain dish to a syrupy consistency; evaporation three times in succession with 10—20 c.c. of strong nitric acid is then recommended. Finally, the mass is taken up with dilute nitric acid and rinsed into a 100 c.c. flask, when heat is applied to effect complete solution. When cold, two drops of *N*/10-thiocyanate and, if necessary, 1 c.c. of *N*/10-iron-alum are added, and the red colour produced is removed by addition of *N*/10-silver nitrate. After again adding a little thiocyanate, the liquid is made up to the mark, shaken, and filtered.

Twenty-five c.c. of the solution are now mixed with 17 c.c. of strong nitric acid, cooled to 18°, and shaken for fifteen minutes with 1—1.25 grams of bismuth peroxide. After cooling for a few minutes by a stream of cold water, the liquid is filtered through a tube, the bottom of which is a perforated porcelain plate covered with asbestos, and the residue is well washed. The permanganate formed is now estimated in the usual manner by means of standardised solution of hydrogen dioxide, the excess of which is titrated with standard permanganate.

L. DE K.

Estimation of Iron in Water. OTTO MAYER (*Mon. Sci.*, 1913, 3, I, 81).—A detailed description of two modifications of a method for the colorimetric estimation of iron in water, based on the action of potassium thiocyanate on ferric salts, the intensity of the colour obtained being compared with those of standard solutions of ferric thiocyanate.

F. M. G. M.

The Quantitative Separation of Iron and Chromium. FRANÇOIS BOURION and A. DESHAYES (*Compt. rend.*, 1913, 156, 1769—1771).—By submitting a mixture of chromic and ferric oxides, heated gradually from 200—650°, to the action of a slow current of chlorine charged with sulphur dichloride vapour, a mixture of the chlorides is obtained, from which the ferric chloride alone is extracted by cold water. This method is applicable to mixtures not containing more than 30% of chromic oxide. With more than this percentage, an equal volume of powdered ammonium sulphate must be added to the mixed oxides before chlorination, which is then conducted at first at a low temperature, finally heating the mixture gradually up to 650°. This method gives very accurate results up to 80% of chromic oxide.

W. G.

Iodometric Estimation of Free and Combined Chromic Oxide. MAX GRÖGER (*Zeitsch. anorg. Chem.*, 1913, 81, 23—242).—Chromites may be brought into solution by Storer's method of treatment with concentrated nitric acid and potassium chlorate (*Zeitsch. anal. Chem.*, 1870, 9, 71). The subsequent precipitation as barium chromate is unsatisfactory, and the good results obtained

by Pearson (*ibid.*, 108) are due to a compensation of errors, the solubility of barium chromate in ammonium acetate solution being balanced by the retention of barium chloride by the precipitate.

The substance containing not more than 0.3 gram of chromium oxide is warmed on the water-bath with 10 c.c. of nitric acid, D 1.4, adding one gram of potassium chlorate gradually in the course of an hour. The solution is then boiled for an hour to expel chlorine, cooled, and diluted to 250 c.c., of which 50 c.c. are titrated immediately, and a further 50 c.c. evaporated to dryness and re-dissolved before titration, as a check on the complete expulsion of chlorine.

For the titration, 50 c.c. of dilute sulphuric acid (4%) and 10 c.c. of potassium iodide solution (10%) are added, diluting with 100 c.c. of water after five minutes. The final colour change, in presence of starch, is from pure blue to bluish-green, and is very sharp. Copper and iron must be removed by boiling with potassium hydroxide and filtering before titration. Manganese must be absent, and the method fails to dissolve natural chromite.

C. H. D.

Separation of Chromium and Manganese. W. CORNELIUS (*Pharm. Zeit.*, 1913, 58, 427).—The metals should be first converted into alkali permanganate and dichromate. On warming the dilute solution on the water-bath with sodium nitrite the manganese is completely precipitated as hydrated peroxide, which is then, after thorough washing with boiling water, converted by ignition over the blowpipe into manganomanganic oxide.

The filtrate containing the chromate is then acidified with hydrochloric acid, when the liberated nitrous acid causes instant reduction of the chromate. The chromium is then precipitated with ammonia as hydroxide, and ignited to oxide.

L. DE K.

Separation of Chromium and Manganese. W. DEDERICHS (*Pharm. Zeit.*, 1913, 58, 446).—The metals present are converted into sulphates by evaporation with sulphuric acid and fused with sodium hydroxide and a little sodium peroxide. The mass is then treated with hot water, and the solution heated with more sodium peroxide until the green colour has disappeared and the liquid is of a pure yellow colour. The precipitated hydrated manganese dioxide is well washed with hot water, and finally converted by ignition into manganomanganic oxide.

The chromate is estimated iodometrically as usual after acidifying the filtrate with hydrochloric acid, or may be precipitated by neutralising the solution with nitric acid and adding mercurous nitrate; on ignition the precipitate yields chromic oxide.

L. DE K.

The Simultaneous Estimation of Small Quantities of Titanium and Vanadium Colorimetrically. JOSEPH W. MELLOR (*Trans. Engl. Cer. Soc.*, 1913, 12, 33–35).—When dilute acidified solutions of titanium and of vanadium sulphates, coloured by the

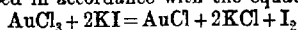
addition of hydrogen peroxide, are measured in a Lovibond's tintometer, making use of the red rays, a straight line curve is obtained for the relation between the concentration of the titanium or vanadium and the tintometer scale. A like relation is found to hold for titanium solutions to which dihydroxymaleic acid (Fenton, T., 1908, 93, 1064) has been added, and, moreover, the colour is not affected by the presence of vanadium. Knowing the above three relations, which must be determined for the particular observation trough used, it is easy to estimate the amounts of titanium and vanadium present in a solution. In part of the solution the amount of titanium is estimated after the addition of dihydroxymaleic acid; this amount is then allowed for in the measurements on the other part of the solution after the addition of hydrogen peroxide.

In the analysis of a silicate the vanadium and titanium oxides are found with the iron and aluminium oxides in the ammonia precipitate. After washing, calcining, and weighing, the mass is fused with eight times its weight of sodium pyrophosphate, and the resulting cake, when cold, is treated by Gooch's process or by the ether process to remove the iron. The solution is acidified with sulphuric acid, and the titanium and vanadium estimated as given above.

T. S. P.

Volumetric Estimation of Gold. VICTOR LENHER (*J. Amer. Chem. Soc.*, 1913, 35, 733—736).—Lenher (this vol., ii, 514) and Diemer (this vol., ii, 515) have found that sulphurous acid is capable of reducing auric chloride to the aurous state in presence of certain other salts. It is now shown that gold can be estimated volumetrically with ease and accuracy by any of the following methods.

(1) Auric chloride is treated with excess of potassium iodide and the iodine liberated in accordance with the equation:



is titrated with standard sulphurous acid. (2) Auric chloride is treated with excess of a strong solution of magnesium chloride and then with potassium iodide, and the iodine is titrated with sulphurous acid. (3) Auric chloride is treated with potassium bromide, and the bromine liberated according to the equation $\text{AuCl}_3 + 2\text{KBr} = \text{AuCl} + 2\text{KCl} + \text{Br}_2$ is titrated with sulphurous acid. (4) Auric chloride is treated with magnesium chloride and potassium bromide, and the bromine is titrated with sulphurous acid (5 and 6). Auric chloride is treated with magnesium chloride or sodium chloride, and the resulting yellow solution is titrated with sulphurous acid until it becomes colourless.

E. G.

Chemistry Applied to Coal Mining. JOHN HARGER (*J. Soc. Chem. Ind.*, 1913, 32, 460—462).—The Home Office method for the estimation of the composition of fire-damps gives correct results only when the inflammable gas present is pure methane. In some fire-damps there appears to be no other inflammable gas, but in many cases the author has found large quantities of heavy hydrocarbons.

By the following method, using the Haldane apparatus, it is possible to estimate the actual volume of inflammable gas without making any assumption as to its composition: (1) In one portion of the sample the carbon dioxide and oxygen are estimated and the volume of residual inflammable gas plus nitrogen noted. (2) In a fresh portion the carbon dioxide is estimated; the inflammable gas is burned, the carbon dioxide formed is absorbed, and then the residual oxygen and the volume of residual nitrogen noted. From (1) the inflammable gas plus nitrogen, and (2) the nitrogen, the volume of inflammable gas is ascertained. This method also gives the amount of oxygen used, which is very important as a check on the other figures.

An improved method for estimating the inflammable gas is as follows: The carbon dioxide and oxygen are first estimated, and the residual mixture of nitrogen and inflammable gas is driven into the combustion pipette, which contains, instead of the simple platinum spiral, one covered with copper oxide. The spiral is heated by an electric current in the usual way, and the inflammable gas converted into carbon dioxide and water. The remainder of the procedure is as usual.

Bog iron ore acts as a very strong catalyst for the preparation of inert gas free from carbon monoxide. In the presence of a small quantity of oxygen the combustion of the last traces of carbon monoxide is affected at 200° or over. A mixture of hydrogen and air burns at 100° when passed over bog iron ore. This ore can be used instead of palladium preparations in gas analysis.

In the absence of air, carbon monoxide is burnt by copper oxide at temperatures below 100° ; hydrogen at one or two degrees above 100° and rapidly at 150° , whilst methane is apparently untouched at these temperatures. The use of copper oxide at 150° is suggested for removing hydrogen from methane when the latter is required pure, and also for estimating hydrogen in the presence of methane.

The presence of carbon dioxide in moderate amount does not appear to influence the combustion of liquid, gaseous, or solid combustibles, but in certain cases, for example, with coal dust, it does seem to exercise a profound influence on the starting of such combustions.

T. S. P.

Analytical Methods for Petroleum. P. S. SADTLER (*J. Ind. Eng. Chem.*, 1913, 5, 393—394).—The quantity of oxygen in petroleum and asphalts may be estimated by burning the substance in an atmosphere of hydrogen and collecting and weighing the water produced. A silica tube is used for the combustion, the further end of the tube being packed with iron-wool; at the beginning of the operation this is heated to bright redness, and hydrogen is passed through the tube until the calcium chloride tube attains a constant weight. The portion of the combustion tube containing the sample is then heated whilst the current of hydrogen is maintained. A U-tube packed with glass-wool is placed between the combustion tube and the calcium chloride tube, and serves to condense vapours other than that of water. A blown petroleum residuum, or so-called

artificial asphalt, was found to contain 3.88% of oxygen when analysed by this method.

W. P. S.

Distinction Between Light Petroleum and So-called "Pine-Benzines" (Turpentine Substitutes) by means of Distillation and Solubility Tests. DAVID HOLDE (*Chem. Zeit.*, 1913, 37, 610—611).—When light petroleum is distilled in an Engler flask the difference in temperature at the beginning of the distillation, as shown by two thermometers, the bulb of one of which is immersed in the boiling liquid whilst the bulb of the other is opposite the exit tube, is usually from 30° to 40°; in the case of turpentine substitutes this difference is generally from 5° to 14°, and in a few instances amounts to 18°. A mixture of 1 vol. of light petroleum with 3 vols. of 96% alcohol always yields a turbid fluid, whilst in the case of turpentine substitutes the mixture is clear.

W. P. S.

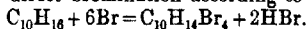
Quantitative Estimation of Light Petroleum in Turpentine. (Miss) C. BAKKER (*Chem. Weekblad*, 1913, 10, 420—425).—The adulterated sample is agitated with concentrated sulphuric acid, and after keeping for twenty-four hours the upper layer is agitated with fuming nitric acid. It is then distilled with steam, and the volume of the light petroleum is measured directly.

A. J. W.

The Maumène Number of Turpentine Oil. CARLO GRIMALDI and L. PRUSSIA (*Chem. Zeit.*, 1913, 37, 657).—When 20 c.c. of turpentine oil are mixed in a vacuum jacketed vessel with 10 c.c. of a freshly prepared mixture of 1 vol. of sulphuric acid, D 1.84, with 7.5 vols. of isomyl alcohol, a rise in temperature of from 77° to 85.7° is observed; the fraction of the oil boiling between 155° and 156° gives a similar Maumène number. Substitutes for turpentine oil (pine oils, etc.) yield numbers which lie below 47°, whilst petroleum oils show practically no rise in temperature with the test.

W. P. S.

Estimation of Caoutchouc by Bromination. WILHELM VAUBEL (*Gummi Zeit.*, 1912, 26, 1879—1880. Compare Esch, A., 1911, ii, 946).—A description of a rapid method for the estimation of caoutchouc by direct bromination according to the equation:



The caoutchouc (2 grams) is dissolved in carbon tetrachloride, the solution treated with potassium bromide (5 grams) and 200 c.c. of dilute hydrochloric acid (1:10), followed by 40 c.c. of a standard solution of 2% potassium bromate; a particle of potassium iodide is added, and the iodine set free titrated in the usual manner.

F. M. G. M.

Direct Estimation of Caoutchouc by Titration of Bromine. FRANZ KIRCHHOF (*Gummi Zeit.*, 1913, 27, 9).—The author discusses Vaubel's method (preceding abstract) of analysing caoutchouc by estimating the excess of free bromine after bromination, and does not consider it satisfactory.

F. M. G. M.

New Method for the Direct Estimation of Caoutchouc. L. G. WESSON (*J. Ind. Eng. Chem.*, 1913, 5, 398).—The method depends on the conversion of the caoutchouc into its nitrosite derivative and the estimation of the carbon in the latter, the quantity of caoutchouc being calculated from the amount of carbon found. The sample is extracted with acetone, and then dissolved or allowed to swell up in carbon tetrachloride; nitrous gases are passed through the solution to saturation, and the nitrosite formed is dissolved in acetone, from which it is separated by precipitation or evaporation. The quantity of carbon is then estimated in the nitrosite by combustion.

W. P. S.

Adapted Wiley Extractor for Caoutchouc Extractions. CHARLES P. FOX (*J. Ind. Eng. Chem.*, 1913, 5, 417).—In place of the usual reservoir, a large glass tube may be substituted; large charges of thin sheet caoutchouc rolled on fabric may be inserted in this tube, which is fitted below the condenser within range of the drip of the condensed solvent.

W. P. S.

Estimation of Nitrogen in Caoutchouc. WALTER SCHMITZ (*Gummi Zeit.*, 1912, 26, 1877—1879).—The author considers the Kjeldahl method to be the most satisfactory for the estimation of nitrogen in caoutchouc. The caoutchouc (2—3 grams) is heated in a 300 c.c. Kjeldahl flask with 45—50 c.c. of concentrated sulphuric acid, with the subsequent addition of copper oxide and potassium sulphate. The distillation of the ammonia can be carried out by (1) direct heating, (2) by the help of a current of steam, or (3) with the aid of a current of air, whilst for the final estimation of ammonium sulphate, potassium iodate and potassium iodide with subsequent titration of the freed iodine is suggested; or sodium oxalate or carbonate can be employed.

F. M. G. M.

Estimation of Nitrogenous By-products in Raw Caoutchouc. ALEXANDER TSCHIRCH and WALTER SCHMITZ (*Gummi Zeit.*, 1912, 26, 2079—2080. Compare Utz, A., 1912, ii, 1002).—A preliminary account of a method by which crude Para caoutchouc is prepared for the estimation of nitrogen. The caoutchouc (2·5 grams) is neither washed nor freed from resin, but after drying in a vacuum desiccator is heated at 80° with 40—60 c.c. of pentachloroethane, cooled, diluted with chloroform, and the solution filtered; the nitrogen estimations are carried out on the residue, and the contents of the filtrate by the Kjeldahl method.

F. M. G. M.

[Examination of Drinks and Animal Organs Suspected to Contain Wood Spirit.] FRANCESCO OLIVARI (*Chem. Zentr.*, 1913, i, 780; from *Arch. Farmacol. speriment.*, 1913, 15, 83—96).—See this vol., i, 797.

Estimation of Methyl and Ethyl Alcohols in Mixtures Containing Both. JULIUS MEYERFELD (*Chem. Zeit.*, 1913, 37, 649—651. Compare A., 1912, ii, 1103).—The dichromate

method for the estimation of methyl and ethyl alcohols yields trustworthy results in the case of the alcohols themselves, and also in mixtures of the same provided that the difference in density of the two alcohols is taken into account in calculating the respective quantities of the alcohols from the amount of dichromate consumed.

W. P. S.

Estimation of Glycerol in Fermented Liquids. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. Chim. Sucr. Dist.*, 1913, 30, 743—749).—One hundred c.c. of the liquid are treated with about 2 grams of lead hydroxide, heated to remove alcohol and other volatile substances, then neutralised with potassium hydroxide, and filtered; the filtrate and washings together should have a volume of 50 c.c. The filtrate is now distilled under reduced pressure at a temperature of 60°, a current of steam being passed through the distillation flask towards the end of the distillation. The distillate containing the glycerol is then concentrated to a volume of about 40 c.c., and the glycerol is estimated by the well-known dichromate method.

W. P. S.

Identification of Phenol by Bromine Water. OTTO ANSELMINO and A. MANDKE (*Chem. Zentr.*, 1913, i, 1543—1544; from *Apoth.-Ztg.*, 1913, 28, 214).—Bromine water produces a white turbidity with phenol in the extreme dilution of 1 to 38,000.

J. C. W.

Effect of Temperature, Acid Concentration, and Time on the Bromination of Phenol for Quantitative Estimations. L. V. REDMAN, A. J. WEITH, and F. P. BROCK (*J. Ind. Eng. Chem.*, 1913, 5, 389—393).—Having investigated the bromination method for the estimation of phenol, the authors recommend the following procedure: Fifty c.c. of water, 5 c.c. of hydrochloric acid, D 1.2, and 15 c.c. of the phenol solution under examination (this solution should not be stronger than $N/10$) are placed in a stoppered bottle, and $N/10$ -bromide-bromate solution (2.76 grams of potassium bromate and 15 grams of potassium bromide per litre) is added with continuous shaking until the contents of the bottle exhibit a slight yellow colour; the temperature of the liquid should be about 22°. After shaking for one minute, 0.5 c.c. of a 20% potassium iodide solution is added, the mixture is shaken for another minute, and the iodine then titrated with $N/10$ -thiosulphate solution. Each c.c. of $N/10$ -bromide-bromate solution corresponds with 0.0015675 gram of phenol.

W. P. S.

Estimation of Phenol in the Presence of Organic Matter. E. MOORE MUNFORD (*Chem. News*, 1913, 107, 253).—A method for the estimation of phenol in such substances as the media used in bacteriology consists in sulphonating the phenol, nitrating the phenolsulphonic acid, and converting the resulting product into ammonium picrate, the quantity of the latter being then estimated colorimetrically. A quantity of the solution under examination is heated to 90° with a few c.c. of sulphuric acid; 10% potassium

nitrate solution is then added, and the mixture is boiled until all organic matter has been destroyed. After cooling, the solution is rendered alkaline with ammonia, and the coloration obtained compared with that yielded by a known amount of phenolsulphonic acid which has been nitrated and treated with ammonia.

W. P. S.

Estimation of Quercetin in Wine. THEODORE VON FELLEBERG (*Chem. Zentr.*, 1913, i, 1366; from *Mitt. Lebensmitt. Hyg.*, 4, 1—14).—The foliage of the vine contains quercetin, 1 kilo. of the fresh shoots yielding 0.17 gram (compare Neubauer, A., 1873, 933). Wine, however, contains the substance in the form of its methyl-pentosan, quercitrin. The yellow dye in wine can be estimated by dyeing-out on mordanted wool and matching against standards. The brownish-red dye in red wine is first removed by unmordanted wool. The dye is developed by fermentation, especially of the grape husks, and can be increased by boiling the husks or the wine with dilute sulphuric acid. Any parts of the vine which are, or have been, green will furnish the dye on warming with dilute sulphuric acid, so that it seems to consist of quercetrin, quercetin, and a decomposition product of a substance allied to chlorophyll.

J. C. W.

Estimation of the Bromine Absorption of Wine. THEODORE VON FELLEBERG (*Chem. Zentr.*, 1913, 1367—1368; from *Mitt. Lebensmitt. Hyg.*, 4, 14—41).—A standard solution containing potassium bromate and bromide has been applied to the estimation of three "bromine numbers": *A*, the bromine absorbed by the original wine; *B*, that required by the residue after distilling off the alcohol and precipitating with lead acetate; and *C*, the bromine required after shaking the concentrate with basic lead acetate. *A—B* gives a measure of the true tanning materials, such as tannin, and also of the dyes (see preceding abstract); *B—C* represents those chlorophyll-like substances which absorb bromine; and *C* is accounted for by those substances which give a colour reaction with vanillin and hydrochloric acid (this vol., ii, 78). The author hopes to be able to apply the process to the detection of sophistication.

J. C. W.

Convenient Quantitative Method of Estimation of Pentoses in Presence of Other Sugars by means of Spectral Observations. ERW. PINOFF and K. GUDE (*Chem. Zeit.*, 1913, 37, 621).—The method is based on Tollens's reaction for the pentoses, the reaction being carried out in alcoholic solution. The coloured solution is then diluted with alcohol until the red and yellow absorption bands are just on the point of disappearing when 20 c.c. of the alcoholic solution is submitted to examination in a cylindrical tube of 3 cm. internal diameter.

Twenty-five c.c. of the pentose solution, containing not more than 3% of pentoses, are mixed with 25 c.c. of hydrochloric acid (D 1.19), 50 c.c. of 96% alcohol, and 0.6 gram phenylglucinol.

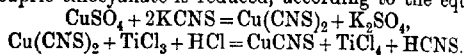
VOL. CIV. ii.

The solution is heated to boiling on a water-bath in a flask provided with a reflux condenser, the boiling continued for half an hour after which the solution is rapidly cooled. If n volumes of alcohol are required for the dilution of one volume of the resulting solution in order to reduce the intensity of the absorption bands so that they can just be recognised under the above conditions, then the percentage of pentose in the solution submitted to examination is given by $4(n+1)0.0237$. If $n=0$, this represents 0.0948%, and this is the smallest quantity which gives rise to recognisable absorption bands.

Experiments with solutions containing dextrose, laevulose, and sucrose, together with pentose, have shown that these substances do not interfere with the estimation.

H. M. D.

Volumetric Application of Titanium Chloride to the Estimation of Invert Sugar. LEOPOLD RADLBERGER and WILHELM SIEGMUND (*Chem. Zentr.*, 1913, i, 1307—1308; from *Österr.-ung. Zeitsch. Zucker-Ind. Landw.*, 1913, 42, 34—44).—The method resolves itself into an estimation of the unreduced copper left in a known volume of Fehling solution. The solution is filtered, made up to 500 c.c., and aliquot parts are acidified, treated with potassium thiocyanate and a little ferric chloride, and titrated in the cold in a carbon dioxide atmosphere with titanium chloride, made by boiling 100 c.c. of the 15% solution with 100 c.c. of concentrated hydrochloric acid and diluting to two litres with air-free water. The reduction of the red ferric thiocyanate does not occur until all the cupric thiocyanate is reduced, according to the equations:



The standardisation of the titanium chloride is effected as follows. The copper sulphate solution is estimated electrolytically, and then 25 c.c. are mixed with 25 c.c. of the Rochelle salt solution, and made up to 500 c.c. Twenty-five, 50, and 100 c.c. are mixed with 2, 4, and 8 c.c. sulphuric acid (D 1.16), 10, 20, and 40 c.c. 10% potassium thiocyanate, and 0.5 c.c. ferric chloride (equivalent to 0.1 c.c. titanium solution), and titrated until the red colour disappears. These conditions are observed for all titrations. The end-point is very sharp, and the method is rapidly carried out and gives good results.

J. C. W.

Aluminium Hydroxide as a Protein Precipitating Reagent in the Estimation of Lactose in Milk. WILLIAM H. WELKER and HOWARD L. MARSH (*J. Amer. Chem. Soc.*, 1913, 35, 823—824).—Experiments are described which indicate that moist aluminium hydroxide can be employed with advantage for the removal of proteins from milk in the process of estimating lactose (compare Marshall and Welker, this vol., ii, 568). The results are not affected by the use of an excess of the reagent, and filtration takes place more rapidly than in the case of the copper-alkali method.

E. G.

Estimation of Milk Sugar in Milk by Precipitation with Ammonium Sulphate. ERICH KRETSCHMER (*Zeitsch. physiol. Chem.*, 1913, 85, 286—291). Compare Salkowski, A., 1912, ii, 610).—Salkowski's method of estimating milk sugar in milk with the polarimeter after precipitation of the proteins with ammonium sulphate has been compared with a number of other processes. * It gives accurate results, and is very suited for rapid working.

E. F. A.

Polarimetric Estimation of Sucrose in Honey by the Lehmann-Stadlinger Method. E. J. SARIN (*Zeitsch. anal. Chem.*, 1913, 52, 367—371).—The author has found the above process to be quite suitable for the technical assay of honey. The process is based on the difference in rotation before and after inversion of the honey. Using a 10% solution, and observing the rotations at 20° in a Schmidt-Haensch apparatus, the difference in the observations is multiplied by 0.5725; result = sucrose.

L. DE K.

The Polarimetric Estimation of Starch in Barley. E. SCHWARZ (*Zeitsch. ges. Brauwesen*, 1913, 36, 85—88, 97—102).—The author discusses the work of Lintner (A., 1908, ii, 1077), and describes numerous experiments carried out under different conditions, from which he finds the specific rotation of barley starch to vary between $[\alpha]_D + 198^\circ$ and $[\alpha]_D + 202.43^\circ$, according to the acid employed, the temperature, and period of the reaction.

F. M. G. M.

Polarimetric Estimation of Starch in Potatoes. FRANZ HERLES (*Zeitsch. Zuckerind. Böhm.*, 1913, 37, 466—471).—The rotatory power of pure potato starch was estimated by stirring weighed amounts of the fine powder with 25 c.c. of water and adding 25 c.c. of fuming hydrochloric acid (D 1.188); after one hour it is diluted to 100 c.c. To produce 100% polarisation the amount of dry, ash-free starch was found to be 8.821 grams; $[\alpha]_D^{20} + 196.25^\circ$.

To estimate the starch in potatoes, 8.82 or 8.80 grams (for Mohr's or for metric c.c. respectively) of very finely pulped substance are washed with 25 c.c. of water into a 100 c.c. flask, and treated with 25 c.c. of the fuming hydrochloric acid (D 1.188). After an hour it is diluted to 100.35 c.c., filtered, and polarised. The reading gives the percentage of starch direct.

When the potatoes are supposed to contain sugar, or other polarising substances, the usual amount is transferred to a 100 c.c. flask and diluted with water to 100.35 c.c. A portion of the filtrate (50 c.c.) is then treated with 25 c.c. of fuming acid in another flask, diluted to 100 c.c., and polarised.

In the case of meals and finely crushed cereals, it is advisable to employ phosphotungstic acid.

N. H. J. M.

Estimation of Glycogen in Muscle. HENRI BIERRY and (Mme.) Z. GATIN-GRUZEWSKA (*Compt. rend.*, 1913, 156, 1491—1493).—The method for the estimation of glycogen in liver (compare this vol., ii, 160) is applicable for its estimation in muscle. The fresh

meat is taken without any prior extraction and digested with potassium hydroxide solution (35%), the glycogen so dissolved is hydrolysed with hydrochloric acid, and the dextrose estimated after precipitation of the proteins with mercuric nitrate. W. G.

Detection of Acetaldehyde in Paraldehyde. GEORGE HETL (Chem. Zentr., 1913, i, 1363—1364; from *Apoth. Zeit.*, 1913, 28, 165—166).—Pure paraldehyde does not give the Gentian-blue coloration with sodium nitroprusside and piperidine (Lewin, A., 1900, ii, 179), but traces of acetaldehyde do react. The coloration is transient, but may be used to determine whether the paraldehyde is up to the official standard. J. C. W.

The Detection and Estimation of Formic Acid. HEINRICH FINCKE (*Biochem. Zeitsch.*, 1913, 51, 253—287).—Steam is passed first through a flask containing the liquid under examination, and the steam and other volatile products are then passed through a second heated flask containing a suspension of calcium carbonate, which neutralises the formic acid. When all the formic acid has been distilled over, the distillate in the second flask is filtered and concentrated, and the formic acid is then estimated by heating the slightly acid liquid with mercuric chloride in the presence of sodium chloride and sodium acetate. The reaction proceeds according to the equation:



The mercurous chloride thus formed is weighed. Certain precautions must be taken when the following acids are present in the distillate: sulphurous, sorbic, glyoxylic, lævulic, cinnamic, salicylic, and fumaric acids. The first-named is oxidised by hydrogen peroxide, the excess of which is destroyed by mercuric oxide. Methods are also given for eliminating errors due to the other acids, which occur, however, only seldom. Formic acid is also formed as a decomposition product of sugars, etc., which may be present in the substance under examination. In this case formic acid will be continuously formed during the distillation, and this fact affords a method for ascertaining whether the acid is a decomposition product, or exists preformed. The experimental methods are given in detail, and the steam distillation apparatus is figured in the text.

S. B. S.

Detection of Formic and Acetic Acids. Application in the Analysis of Glycerol. LÉO BONNES (Chem. Zentr., 1913, i, 1364; from *Bull. Sci. Pharmacol.*, 1913, 20, 99—101).—The liquid is boiled down to one-quarter with sulphuric acid, the distillate neutralised with calcium carbonate, evaporated to dryness without filtering, and then submitted to dry distillation. The distillate is tested for aldehyde with Leys's magenta-bisulphite solution, and for acetone by means of Legal's sodium nitroprusside reaction.

J. C. W.

Estimation of Lactic Acid. A. BELLÉ (Bull. Soc. chim., 1913, [iv], 13, 565—572 *).—The method is intended for the estimation of

and *J. Pharm. Chim.*, 1913, [vii], 8, 21—29.

lactic acid in presence of much organic matter, and involves (1) the elimination of proteins, (2) extraction of the lactic acid by means of ether, and (3) estimation of the acid by conversion into acetaldehyde, and determination of the latter by means of ammoniacal silver nitrate.

For the removal of proteins, Patein and Dufau's reagent is used, which leaves the lactic acid in the mother liquor in the form of sodium lactate. The mother liquor is evaporated to syrupy consistence, mixed with 1 or 2 c.c. of 20% sulphuric acid, and then with enough dry washed sand to enable it to be packed in a Soxhlet extractor of slightly modified form and extracted with dry ether. The partly purified lactic acid thus obtained is carefully oxidised in a special apparatus with permanganate, and the acetaldehyde formed aspirated into a known volume of ammoniacal silver nitrate of known strength. When the reaction is complete the un-reduced silver is determined by the Charpentier-Volhard method. The apparatus used is figured in the original, which also gives exact experimental details and a series of typical results. T. A. H.

The Estimation of Lactic Acid in Urine. MAX DAPPER (*Biochem. Zeitsch.*, 1913, 51, 398—406).—Lactic acid cannot be estimated directly in urine by the method of von Fürth and Charnass, but the urine must be first concentrated, and the acid extracted by ether. The details of the manipulation are described, and estimations of lactic acid from various pathological cases are quoted. S. B. S.

Detection of Hydrocyanic Acid. C. PERTUSI and E. GASTALDI (*Chem. Zeit.*, 1913, 37, 609—610).—The test proposed depends on the blue coloration or precipitate which is obtained when copper acetate, potassium cyanide, and benzidine acetate are mixed together in solution. The reaction is also given by other substances, and is only characteristic of hydrocyanic acid under the following conditions. After the removal of metals from the solution under examination, the latter is boiled with sodium carbonate, filtered, and carbon dioxide is passed into the filtrate; this is then added to a mixture consisting of 1 drop of a 3% copper acetate solution, 1 c.c. of a 10% disodium phosphate solution, and 4 drops of a saturated benzidine acetate solution. The test will detect 0.007 mg. of hydrocyanic acid in 10 c.c. of solution. W. P. S.

Detection of Benzoic Acid in the Presence of Phenols and Salicylic Acid. LUCIEN ROBIN (*Ann. Falsif.* 1913, 6, 277—278).—As phenol, salicylic acid, etc., yield a red coloration when submitted to the test for benzoic acid described previously by the author (*A.*, 1908, ii, 1078), the test must be modified in order to remove the influence of these substances. For this purpose the residue of benzoic acid extracted from the material under examination is dissolved in water, the solution is acidified with sulphuric acid, heated to 80°, and treated with potassium permanganate; this

destroys any phenol or salicylic acid which may be present, and the benzoic acid is then extracted and identified as described.

W. P. S.

The Estimation of Benzoic Acid in Milk. JOHN F. LIVERSENGE and NORMAN EVERS (*J. Soc. Chem. Ind.*, 1913, 32, 319—320).—A milk preservative is now on the market, consisting of a mixture of sodium benzoate and sodium carbonate, and the authors have consequently investigated methods for the detection and estimation of benzoic acid in milk. It was found that if a solution of sodium benzoate is acidified with sulphuric acid, distilled with steam, and the distillate extracted with ether, all the benzoic acid could not be recovered. Also, in the case of milk containing no benzoic acid, the steam distillate, when acidified and extracted with ether, yielded a certain residus.

The following empirical method, by means of which about 45% of the benzoic acid is obtained, is recommended: 100 c.c. of the milk are mixed with 10 c.c. of concentrated sulphuric acid, and distilled in a current of steam until 600 c.c. have passed over. The distillate is acidified with 5 c.c. of concentrated hydrochloric acid, and extracted successively with 100, 35, and 35 c.c. of ether, after which the ether is allowed to evaporate and the residue weighed after drying for twenty-four hours in a desiccator; 5 mg. are subtracted from the weight to correct for the blank obtained with milk free from the preservative in question.

A modification of Halphen's test (A., 1908, ii, 906) for benzoic acid is also recommended as giving fair quantitative results. To the residue from the ethereal extract are added 1 c.c. of concentrated sulphuric acid and 0.2 c.c. of concentrated nitric acid, and the dish heated, so that it fumes moderately for three minutes, unless a deep yellow colour forms, when the heating is stopped at once. When cool, 5 c.c. of water are added, and the liquid poured into a 50 c.c. Nessler cylinder, washing the dish with about 3 c.c. of water. One c.c. of a saturated solution of sodium sulphite is then mixed with the liquid, and afterwards 10 c.c. of 6*N*-ammonia. A brown colour indicates benzoic acid. Two c.c. of ammonium sulphite are then added, producing a deep red colour, the solution is diluted to 50 c.c., and the colour compared with standards prepared in the same manner.

T. S. P.

Estimation of Glycyrrhizic Acid in Sweetmeats and in Liquorice Juice. E. DURIER (*Ann. Falsif.*, 1913, 6, 252—255).—Twenty grams of the sample are dissolved in 50 c.c. of 10% ammonia, and 150 c.c. of 95% alcohol are added gradually; after the lapse of about five hours, the precipitate is separated by filtration, and washed with about 100 c.c. of 70% alcohol. The filtrate and washings are evaporated to dryness, the residue is dissolved in 50 c.c. of water and 1 c.c. of ammonia, the solution is acidified by the addition of 2 c.c. of hydrochloric acid, and set aside for twenty-four hours. The precipitate is then collected on a filter, washed with 25 c.c. of water, dried partially, dissolved in

ammonia, the solution evaporated, and the residue weighed; 0.320 gram of ammonium glycyrrhizate corresponds with 4 grams of liquorice juice, the minimum quantity which, according to French law, should be present in 100 grams of liquorice sweetmeats. To the quantity of ammonium glycyrrhizate found, however, must be added 23 mg. to correct for the solubility of the compound. In the case of liquorice juice (sticks), 2 grams are taken for the estimation, and it is necessary to make repeated extractions with alcoholic ammonia in order to obtain the glycyrrhizic acid in solution.

W. P. S.

Comparative Investigation of Different Methods for the Estimation of Uric Acid. LUCIEN BERNARD (*Chem. Zentr.*, 1913, i, 1364; from *Bull. Sci. Pharmacol.*, 1913, 20, 65-69).—The author finds that Salkowski's method (A., 1895, ii, 538) gives the best results.

J. C. W.

The Titration of Uric Acid in Urine after Precipitation with Silver Reagent. ERICH KRETSCHMER (*Biochem. Zeitsch.*, 1913, 50, 223-232).—For clinical purposes, uric acid can be estimated with sufficient accuracy and rapidly, by precipitating it by Salkowski's method as magnesium silver urate; the precipitate is first treated with sulphuric acid, the precipitated silver sulphate is filtered off, and the filtrate is then titrated with $N/20$ -potassium permanganate solution. The values obtained by this method were somewhat too high, and this is due to the fact that the purine substances are also precipitated and obtained in a form in which they are completely oxidised by permanganate.

S. B. S.

Estimation of Uric Acid in Urine and Blood. JULIUS SCHNELLER (*Chem. Zentr.*, 1913, i, 1234; from *Zeitsch. exp. Path. Ther.*, 1913, 12, 341-347).—To avoid the loss of uric acid, which is carried down in precipitating the protein, it is converted into its soluble formaldehyde compound. For this purpose, 100 c.c. of blood are introduced into 1 litre of water containing 10 grams of acid potassium phosphate and 10 c.c. of 40% formaldehyde, previously neutralised with sodium carbonate. After separation of the protein, the solid filtrate is concentrated to 100 c.c., and 2 grams of sodium acetate and 10 c.c. of commercial sodium hydrogen bisulphite solution are added. The mixture is then heated, and 10 c.c. of 70% copper sulphate are added. The precipitated copper compound is decomposed by hydrogen sulphide, 10 c.c. of hydrochloric acid are added, and the liquid, after filtration, is concentrated. For quantitative work a further precipitation with ammoniacal silver nitrate is recommended.

S. B. S.

Precipitation of Uric Acid and Purine Bases by Zinc Salts. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, 85, 346).—Both the uric acid and purine bases of urine are completely precipitated by zinc salts. In concentrated acid urine zinc salts occasion a slight flocculent precipitate of zinc phosphate, which

slowly becomes crystalline, and may then be easily mistaken for uric acid.

E. F. A.

Some Peroxydase Reactions of Milk. TEMISTOCLE JONA (*Chem. Zentr.*, 1913, i, 1790—1792; from *Arch. Farmacol. experim.*, 1913, 15, 122—130).—The usual preservatives do not influence the peroxydase reactions with guaiacol or *p*-phenylenediamine and hydrogen peroxide for the discrimination between fresh and boiled milk. Ammoniacal copper sulphate is not a good preservative, but milk which had been kept at -10° gave a good reaction. On heating the milk, the peroxydase reaction failed earlier with the preserved than with the fresh samples, salicylic acid and mercuric chloride being most marked in this respect. The reaction is influenced by acids in quite different ways, and since the failure of the reaction with old milk depends on the development of acids, it cannot be used to determine the age of the sample.

J. C. W.

The Oxidation-Number of Milk. TEMISTOCLE JONA (*Chem. Zentr.*, 1913, i, 1234; from *Giorn. Farm. Chim.*, 1913, 62, 59—63. Compare A., 1911, ii, 233).—The number of c.c. of 0.1*N*-potassium permanganate required for the oxidation of 1 c.c. of milk is called the "oxidation number," and should be 50 to 52. It is sensibly affected by watering the milk.

J. C. W.

Detection of Sesame Oil. G. F. A. TEN BOSCH (*Pharm. Weekblad*, 1913, 50, 526—527).—The author describes a modification of Kreis's test for sesame oil. One drop of the oil is dissolved in 1 c.c. of light petroleum, benzene, or chloroform, and mixed with 1 c.c. of sulphuric acid containing one-third of its volume of hydrogen peroxide. A green coloration due to the presence of sesamin is developed.

A. J. W.

A Rapid Clinical Method for Estimating Urea in Urine. ELI K. MARSHALL, jun. (*J. Biol. Chem.*, 1913, 14, 283—290).—The urine is treated with extract of soy bean; the urea is by the urease in the extract rapidly converted into ammonium carbonate, and the alkalinity of the solution is then determined by titration, methyl-orange being used as indicator.

W. D. H.

Folin's Microchemical Method for Estimating Urea. JOSEPH C. BOCK (*J. Biol. Chem.*, 1913, 14, 295—298).—In Folin and Farmer's method (A., 1912, ii, 702) the ammonia can be estimated by titration or colorimetrically; titration, however, gives results which are too low. This is due to increase of acidity, which is greater when air is blown through the mixture whilst still hot, and even below room temperature an odour of acetic acid is still noticed. If, however, an extra tube containing strong alkali is introduced so that the air passes through it before going into the standard acid, and the air current is kept up for fifteen minutes, all the acetic acid is retained, and satisfactory results obtained.

W. D. H.

Estimation of Urea in Urine by means of Sodium Hypobromite. MARIE KROGH (*Zeitsch. physiol. Chem.*, 1913, 84, 379—407).—When urea is decomposed with sodium hypobromite part of the nitrogen is set free, and the rest converted into oxides of nitrogen. The carbon is, in part, oxidised to carbon dioxide, and the rest oxidised only to carbon monoxide. The oxidation is the more complete the smaller the proportion of bromine to sodium hydroxide. On adding dextrose, there is still less oxidation, all the nitrogen being eliminated as such, and the greater part of the carbon escaping as monoxide.

Similarly, when ammonium chloride is decomposed by sodium hypobromite, the nitrogen is only in part liberated as such, and the rest as oxides of nitrogen. When dextrose is added, the elimination of nitrogen is lessened, and some of the ammonia is not decomposed, but the total gas evolved is greater as carbon monoxide is set free from the sugar.

The estimation of urea in urine is carried out as follows. After precipitation with phosphotungstic acid and neutralisation, sodium hypobromite is added in the proportion of 1 c.c. of bromine in 24.5 c.c. of 30% sodium hydroxide and 70 c.c. of water. The volume of gas evolved multiplied by 100/96.5 gives the urea nitrogen. When the hypobromite consists of 1 c.c. of bromine in 196 c.c. of 30% sodium hydroxide, the total gas evolved is equal to the urea nitrogen. Duplicate experiments only differ by 1%. The amount of urea so estimated is less than when it is determined by Folin's method.
E. F. A.

A Ureometer for Estimation of Urea in Urine, Blood, and Cerebro-spinal Fluid. The Activity of Kidneys and Liver. HEYNINX (*Biochem. Zeitsch.*, 1913, 51, 355—368).—A ureometer is described by means of which an estimation of urea in 2—10 drops of urine, or 5 c.c. of blood-serum or cerebrospinal fluid, is possible; by this means, it is claimed that it is possible to make a clinical estimation of the activity of the liver. The nitrogen produced by the hypobromite reaction is measured in a small apparatus (which is figured in the text), consisting of two parts—a lower part where the hypobromite reagent is mixed with the liquid under examination, and an upper part, which fits on to this, in which the nitrogen evolved is measured by the displacement of the water in a calibrated tube.
S. B. S.

Precipitating Alkaloids by Lloyd's Reagent. SIGMUND WALDBOTT (*J. Amer. Chem. Soc.*, 1913, 35, 837—838).—Lloyd's reagent for precipitating alkaloids (*Chem. Abstr.*, 1913, 7, 683) consists essentially of hydrated aluminium silicate, and has the composition: H_2O , 17.41; SiO_2 , 55.30; Al_2O_3 , 9.82; Fe_2O_3 , 14.18; CaO , 1.58; CO_2 , not estimated. The activity of the reagent is not destroyed by heating it to 130° , but at a red heat water is expelled, and the reagent becomes inert. If the material is extracted with hydrochloric acid, the residue is still effective. Treatment with concentrated nitric acid or aqua regia does not

impair its activity. The reagent is capable of removing alkaloids completely from neutral or acid solutions, and the alkaloid can be recovered by treating the precipitate with alkali and an alkaloidal solvent. The residue thus obtained is a jelly-like mass which still retains activity towards alkaloids and can also precipitate inorganic salts, such as barium chloride, lead nitrate, and zinc sulphate.

The action is colloidal; it has been found that colloidal silicic acid and colloidal arsenious sulphide are also capable of precipitating quinine sulphate.

E. G.

Controls for the Folin Method of Estimating Creatinine. WILLIAM H. THOMPSON (*Proc. physiol. Soc.*, 1913, i—ii; *J. Physiol.*, 46).—The double picrate of creatinine and potassium was found to act as a more satisfactory control than a solution of creatinine.

W. D. H.

Estimation of "Saccharin" in Foods. JOHANN KARAS (*Zeitsch. Nahr. Genussm.*, 1913, 25, 559—560).—The solution, or aqueous extract of a solid substance, is concentrated, cooled, and treated with about 10 c.c. of a 10% tannin solution and 8 c.c. of basic lead acetate solution. After filtration, the filtrate is acidified with phosphoric acid, the lead phosphate is separated by filtration, and the filtrate is extracted with a mixture consisting of equal volumes of ether and light petroleum. The residue obtained on evaporating the solvent will consist of "saccharin." Substances containing much fat may be rendered alkaline and extracted with ether before the saccharin is extracted with water.

W. P. S.

Method of Distinguishing Natural from Artificial Colouring Matters by Estimating their Electrical Conductivity. W. G. CHLOPIN and P. J. VASSILIEVA (*Zeitsch. Nahr. Genussm.*, 1913, 25, 596—598).—The authors outline a method which depends on the fact that vegetable and animal colouring matters, such as cochineal, catechu, saffron, turmeric, etc., have a much greater electrical resistance than artificial colouring matters; this difference in conductivity is more marked in alcoholic than in aqueous solution. The process will probably be of use in the analysis of mixtures of the two classes of colours.

W. P. S.

New Reaction for the Detection of Aniline Colours in Foods and Especially in Wines. PHILIPPE MALVEZIN (*Ann. Chim. anal.*, 1913, 18, 193).—The reagent is prepared by passing sulphur dioxide into formaldehyde solution; the substance formed, $\text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, yields a violet coloration when mixed with a solution containing a very small quantity of magenta or other aniline colouring matter even when these have been decolorised previously with sulphur dioxide or animal charcoal. The wine to be tested is mixed with a small quantity of animal charcoal, filtered, and a portion of the colourless filtrate mixed with an equal volume of the reagent. If the wine contains magenta or similar colouring,

matter, a violet coloration develops; natural wines yield a faint pink coloration. The test is rendered more sensitive by heating the filtrate with the reagent.

W. P. S.

Identification of Small Amounts of Dyes by Oxidation with Bromine. WALTER E. MATHEWSON (*Chem. News*, 1913, 107, 265).—The test consists in adding to the dye solution twice as much bromine water, drop by drop, as is required to decolorise it, followed by solution of hydrazine sulphate, and finally excess of sodium carbonate solution (A). A second test portion is treated similarly, except that a few drops of α -naphthol solution (10% in 50% alcohol) are added just before making alkaline (B).

Typical examples of the following groups of dyes give the colours mentioned with the tests A and B: *Nitro-dyes*, both yellowish-brown. *Monazo-dyes*, A, colourless, pale olive, blue, or bluish-red; B, red or purplish-red. *Disazo-dyes*, A, brown; B, purple to brown. *Triphenylmethane dyes*, both nearly colourless. *Xanthen dyes*, both red with green fluorescence to bluish-red. *Alizarin*, both purplish-red. *Asine dyes*, both red. *Quinoline dyes*, both yellow to pale brown. *Natural dyes*, both pale yellow to pale brown. The dye should be purified, if necessary, by extracting with amyl alcohol, before applying the tests.

T. A. H.

Detection of Saffron in Farinaceous Foods. CARLO MARTINI (*Boll. chim. Farm.*, 1913, 52, 37–41).—The colour reactions of saffron with sulphuric acid or with nitric acid do not give satisfactory results when they are directly applied to farinaceous matter. A good preliminary indication is afforded by the characteristic aromatic odour produced when the material is boiled with acid. If artificial colouring matters are not present, the suspected material may then be extracted thoroughly with alcohol, the residue after evaporation purified by extraction with ether at least twice, then treated with alcohol again. The residue obtained when this is evaporated yields the fugitive blue coloration with nitric acid. The reaction with sulphuric acid can only be obtained with certainty if the above treatment with ether has been repeated a third time with anhydrous ether, and even then a definite blue coloration is not always seen, but more frequently a green coloration becoming brown. With sulphuric acid a violet coloration appears later, even in the absence of saffron.

R. V. S.

The Triketohydrindene Hydrate [Reaction] (Ruhemann). EMIL ABDERHALDEN and HUBERT SCHMIDT (*Zeitsch. physiol. Chem.*, 1913, 85, 143–147. Compare Abderhalden and Schmidt, A., 1911, ii, 674).—The sensitiveness of the triketohydrindene hydrate reagent depends on the concentration of the reacting products—a blue coloration is often obtained on concentration when it was not at first visible. Fresh milk, urine, saliva, blood plasma, lymph, sweat, fresh and boiled egg-white, fresh and cooked meat when dialysed give up substances which show no biuret reaction, but react with triketohydrindene. A glass rod which has been handled with the

fingers for some time will give a reaction with triketohydrindene. The reagent shows 1 part of glycine in 65,000 and about 1 in 15,000 to 25,000 of the other monoamino-acids. Proteins must be purified by dialysis until the dialysate no longer reacts with the reagent before being used for anaphylaxical studies.

E. F. A.

A Colour Reaction for Proteins. LOUIS LEWIN (*Ber.*, 1913, 46, 1796—1798).—A 0.1% solution of triformoxime (trioximino-methylene) in commercial sulphuric acid gives a pure violet, persistent coloration with proteins. The reaction is very delicate, and takes place with 1 c.c. of a 0.05% solution of egg-albumin or even with diluted saliva. A solution of the reagent in pure sulphuric acid gives a yellow colour, which, however, shows the same absorption band, $\lambda = 536 \mu\mu$. Traces of selenium or, to a lesser extent, arsenic are the cause of the violet coloration. Paraformaldehyde gives similar effects, but it is not so sensitive. Indole and codeine also give characteristic violet or gentian-blue colours, but glue does not respond to the test.

J. C. W.

The Conditions for Precipitation of Albumin by Picric Acid. HENRI LABBÉ and R. MAGUIN (*Compt. rend.*, 1913, 156, 1415—1417).—Using Esbach's citro-picric reagent, the authors have determined the amount of picric acid fixed by varying amounts of ovalbumin during their precipitation by a given volume of the reagent. The process consists in estimating the acidity of the liquid before and after the admixture of the albumin solution. By plotting the weights of albumin used against the amounts of picric acid fixed, the points are found to lie on the branch of a hyperbola, and by means of this curve, in conjunction with two acidimetric titrations, unknown amounts of albumin can be estimated.

W. G.

Estimation of the True Reaction of the Blood by the Electric Method. A. P. KONIKOV (*Biochem. Zeitsch.*, 1913, 51, 200—210).—Attention is called to the influence of the dissolved oxygen and carbon dioxide in the blood when the reaction of the latter is measured electrometrically. The oxygen acts in that it reduces the hydrogen, and the carbon dioxide in that on evolution it increases the alkalinity of the blood. To eliminate the latter effect an apparatus is described, whereby the blood is shaken in the presence of hydrogen, and into the hydrogen-carbon dioxide atmosphere thus produced containing the electrode, fresh blood is introduced (compare Hasselbalch, this vol., ii, 379). The readings are taken when the potential differences are constant, that is, when the evolved oxygen has combined with the hydrogen, which process is accelerated by shaking and warming slightly. If the blood is laked, by alternate freezing and thawing, the acidity is increased. The reaction of the formed elements is therefore different to that of the serum.

S. B. S.

General and Physical Chemistry.

The Optical Properties of Water and its Physical Constitution. C. CHÉNEVEAU (*Compt. rend.*, 1913, 156, 1972—1974).—The author has measured the refractive power of water at 0° and 100°, and finds that the results are in agreement with the hypothesis that water is a mixture, in a proportion varying with the temperature, of two substances, one of which is analogous to ice. Measurements on solutions of different concentrations of potassium chloride at 15° showed that the specific refractive power of the water was constant, although the proportion of "ice" varies with the concentration.

T. S. P.

Relationship between Physical Properties of Solutions. IV. Refraction, Dispersion, and Dissociation of Salts in Water. ADOLF HEYDWEILLER (*Ann. Physik*, 1913, [iv], 41, 499—542. Compare Abstr., 1910, ii, 106, 398; 1912, ii, 433).—The refractive indices of solutions of a number of salts at concentrations from 0.1—4.0 n for sodium light at 18° are given together with the corresponding values for λ_a , λ_p , and λ_v for hydrogen. From these the value for equivalent solutions is calculated by means of the formula $\Delta_n = 100(n - n_0)/mn_0$, in which Δ_n is the refractive index for an equivalent solution, m the molecular concentration of the solution, n_0 the refractive index of water, and n that of the solution. The salts examined consist of a number of acetates, iodates, chlorates, nitrates, thiocyanates, fluorides, chlorides, bromides, iodides, sulphates, chromates, and metasilicates. It is shown that by means of the Δ_n value, which changes only slightly with concentration, n can be calculated for any concentration by means of the expression $n = 1.33327 + 4m/300\Delta_n$. It is shown that Δ_n runs parallel with the corresponding density value Δ_d , and that the following relationship exists between the electro-conductivity and the refraction: $\Delta_n = B_n + (A_n - B_n)i$, in which i represents the electrolytic dissociation, A_n the value of Δ_n for a normal solution of ions, and B_n the corresponding value for a normal solution of undissociated molecules. The values of A_n , B_n , and $(A_n - B_n)$ are calculated for the cases examined. The author calculates a number of ionic moduli for the refraction, on the assumption that the refraction of a dissolved compound is the mean of the sum of the refractions of its ions. Thus $A_n = A_{n_1} + A_{n_2}$, in which A_{n_1} and A_{n_2} are the ion constants. In this way the following values have been obtained: $H' = -119$, $Li = -55$, $Na' = 61$, $Ag' = 679$, $NH_4' = 60$, $K' = 85$, $Rb' = 154$, $\frac{1}{2}Mg' = 208$, $\frac{1}{2}Zn' = 389$, $\frac{1}{2}Cd' = 381$, $\frac{1}{2}Cu' = 421$, $\frac{1}{2}Ca' = 319$, $\frac{1}{2}Sr' = 396$, $\frac{1}{2}Ba' = 495$, $C_2H_5\cdot COO' = 1025$, $CH_3\cdot COO' = 846$, $H\cdot CO\cdot O' = 664$, $IO_3' = 1985$, $BrO_3' = 1254$, $ClO_3' = 778$, $CNS' = 1316$, $NO_3' = 718$, $F' = 480$, $Cl' = 777$, $Br' = 1063$, $I' = 1619$, $OH' = 795$, $\frac{1}{2}SO_4' = 1026$, and $\frac{1}{2}CrO_4' = 1665$. The above

numbers are all multiplied by 1000. It is shown that the cation moduli can be represented with very close approximation by a multiple of the figure 0.029. The author calculates the refraction equivalents of the undissociated and completely dissociated salts by means of the Lorenz-Lorentz formula, and finds generally that the latter quantity is about 3½% larger than the former. The true ionic volumes are calculated from considerations based on the ionic refraction, and the following values for the cross-section of the following ions obtained: $d \times 10^8 =$ H 1.65, Li 1.75, Na 1.93, K 2.38, Rb 2.62, Ag 2.74, Cs 2.93, Tl 3.27, Mg 2.01, Zn 2.38, Cu 2.38, Ca 2.43, Sr 2.62, Cd 2.70, Ba 3.00, Pb 3.46, F 1.39, Cl 2.74, Br 3.15, and I 3.70. From these values it is shown that the true ionic volume is not, like the apparent atomic volume, a periodic function of the atomic weight. It is shown that the dispersion and constitution are related; the author represents the dispersion by $10^8(\Delta_v - \Delta_m)$, and from these values it is shown that the dispersion in the visible spectrum is practically independent of the nature of the cation, and consequently depends practically entirely on the anion. Measurements similar to the whole of the foregoing are recorded for the ultraviolet part of the spectrum. J. F. S.

Band Spectrum of Barium Fluoride in the Electric Arc and Line Spectrum of Barium from 7059—8200 A.U. HANS GEORGE (*Zeitsch. Wiss. Photochem.*, 1913, 12, 237—258).—The band spectrum was measured from photographs by a measuring machine. The spectrum was produced by means of a Rowland concave grating 6.34 metre radius of curvature and 20,000 lines per inch. The incandescent vapour was obtained by filling hollow carbon rods with powdered barium fluoride and feeding the arc with 2.5 amperes at 220 volts. In some cases, to avoid the carbon bands, the carbon electrodes were replaced by copper tubes. Ten visible bands are described, together with one in the infra-red and one due to barium oxide. The line spectrum of barium from 7059 to 8200 is measured with the international normal. Discussion of the previous work and results on this subject is given in the paper. J. F. S.

Displacement of the Spectral Lines of Certain Metals Produced by the Presence of the Vapour of Another Metal. KRIVIN BURNS (*Compt. rend.*, 1913, 156, 1976—1978).—The lines of the spectrum of barium or manganese, as obtained in the spectrum of an arc between iron electrodes containing these metals as impurities, are found to have suffered a displacement, as compared with the lines obtained from an arc between carbon electrodes which have been impregnated with salts of the metals. The same holds for cadmium in the presence of mercury, as, for example, when a quartz lamp containing a cadmium amalgam is used as the source of light.

This phenomenon may possibly account for the differences observed between the wave-lengths of lines in the solar and arc spectra.

It follows that it is not safe to take the wave-lengths of lines due to impurities as spectral standards.

T. S. P.

Method of Observing the Flame Spectra of Halogen Salts. E. N. DA C. ANDRADE (*Proc. London Physical Soc.*, 1913, 25, 230—234).—If metals such as copper, nickel, iron, etc., be held* in a bunsen flame containing chlorine, produced by leading the air supply through chloroform, characteristic colours are imparted to the different zones of the flame. These colours are due to the chlorides of the metals which can exist in the flame undissociated in the presence of excess of chlorine. This method makes it comparatively easy to observe the different emissions which occur in the different zones. The electrical migration of the vapour can also be observed in such flames. All the chloride spectra have common characteristics. Smithells (*Phil. Trans.*, 1900, A, 193, 121) showed that the colour of lithium and strontium flames is destroyed by the presence of chlorine. In such cases the vapours are not electrically charged, whilst in the case of those metals which give coloured flames in the presence of chlorine the vapours are charged. Compound spectra were observed in some cases on introducing wires into flames containing bromine or iodine vapour.

J. F. S.

Different Band Spectra of Mercury. JOHANNES STARK and GEORG WENDT (*Physikal. Zeitsch.*, 1913, 14, 562—566).—It is shown that there are at least three band spectra of mercury. The first is obtained in the positive light of a mercury lamp at a pressure of 1–10 mm. and a current of 10–30 milliamps. It consists of five bands, which have maxima at λ 490 $\mu\mu$ –400 $\mu\mu$,

λ 350 $\mu\mu$ –310 $\mu\mu$,

λ 270 $\mu\mu$ –250 $\mu\mu$, λ 248 $\mu\mu$, and λ 234 $\mu\mu$. The second band spectrum is obtained in the positive light in hydrogen of 10–20 mm. pressure and a current of 12–20 milliamps. This consists of thirteen bands and of three other bands of a quite different nature. A third band spectrum is observed in the negative light, but details of this are reserved for a future publication. The author considers that the first spectrum is caused by the neutral system univalent mercury-ion-electron in the process of recombining to form a neutral atom. The second spectrum is probably due to an electron which is combining with bi- or ter-valent mercury ions. The third spectrum is regarded as being due to either a ter- or quadri-valent mercury ion combining with an electron. J. F. S.

Differentiation between the Mercury Lines λ 2536.7 and 2345.5 Å and the Mercury Bands λ 2540 and λ 2346 Å. JOHANNES STARK and GEORG WENDT (*Physikal. Zeitsch.*, 1913, 14, 567–568. Compare last abstract).—A comparison of the characteristics of the above-mentioned bands and lines is given, which enables the one to be identified in the presence or absence of the other.

J. F. S.

Normal System of Wave-lengths in the Arc Spectrum of Iron. F. GOOS (*Zeitsch. wiss. Photochem.*, 1913, 12, 259—275).—The author points out that in determining the arc spectrum of iron second order, it is not sufficient to say that the arc was using a current between 5 and 10 amperes, but every condition, particularly the pressure, must be characterised. Measurements of Fabry and Buisson, Eversheim, and Pfund are quoted as showing differences which have arisen in the second order iron spectrum from differences in the arc. The normal third order for the iron arc spectrum is discussed. The influence of pressure on the width of lines and the sensitiveness of certain lines to changes in pressure are discussed by the author, and measurements are given. Suggestions are made for the determination of the normal third order for the iron spectrum. J. F. S.

Arc Spectrum of Platinum Measured on the International Normal. ERICH SYMONS (*Zeitsch. wiss. Photochem.*, 1913, 12, 277—295).—The author has photographed and measured the arc spectrum of platinum; the measurements in the region λ 6945— λ 4282 were made on the international normal, and the regions below and above this on Buisson and Fabry's normal measurements. The measurements were made by means of a Rowland concave grating 6.4 metre radius of curvature and 20,000 lines to the inch. The measurements in the region λ 6500— λ 2500 were made on the second order spectrum, whilst those above and below were made on the first order spectrum. The illumination was obtained by placing small pieces of platinum foil in the crater of a carbon arc fed by 5 amperes at 220 volt direct current. A full list of the lines is given, ranging from λ = 6710.44 to λ = 2144.19. These values are compared with the measurements of Rowland and Tatnall, Exner and Haschek, and Kayser. J. F. S.

The Absorption of Water Vapour and New Residual Ray Groups in the Region of Long Wave-lengths. HEINRICH RUBENS (*Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 28, 513—549. Compare A., 1910, ii, 172, 262).—Experiments are made on the influence of water-vapour on the residual rays obtained by reflexion from four surfaces of rock salt, sylvine, and potassium bromide. It is shown that water-vapour has a very marked influence on the energy distribution of the residual rays, and that existence of two maxima in the energy curves of these substances is entirely due to the water-vapour in the atmosphere through which the rays pass. The mean wave-length is but slightly influenced by the presence of water-vapour. The residual rays from silver chloride, lead chloride, calomel, and silver bromide were examined, and shown to have mean wave-lengths of 81.5μ , 91.0μ , 98.8μ , and 112.7μ respectively. The energy distribution curves of these substances also show peculiarities which must, from a study of the interference curves, be attributed to water vapour. Water vapour shows a strong absorption over the spectrum range 45μ — 120μ , with specially strong absorption at 50μ , 66μ , 79μ , and probably also

at 58μ and 103μ . Water vapour is particularly transmissive at 47μ , 54μ , 62μ , 75μ , 91μ , and 115μ . In the region 53μ — 113μ quartz exhibits a strong dichroism in the sense that the residual rays are more strongly absorbed when the electric vector swings at right angles to the axis than when the vector is parallel to the axis.

J. F. S.

The Absorption of Light by Inorganic Salts. IX. Solutions of Copper, Nickel, and Cobalt Salts in Alcohol and Acetone. ROBERT A. HOUSTON and A. H. GRAY (*Proc. Roy. Soc. Edin.*, 1913, 33, 137—146. Compare A., 1911, ii, 785, 786; 1912, ii, 507).—The authors investigate the absorption spectra of the salts of nickel cobalt and copper salts in solution in acetone and alcohol. The measurements are made by means of a spectrophotometer, and are all in the visible region. In many cases, particularly the nitrates, it was impossible to obtain the salts anhydrous owing to decomposition, and in other cases, that is, sulphates, the anhydrous salts were found to be insoluble in alcohol and acetone. In these cases the hydrated salts were used for measurement of the extinction-coefficient, whilst in other cases the anhydrous salts were used. The general result is drawn from the measurements, that when copper, nickel, and cobalt salts are dissolved in acetone or alcohol their absorption is much greater, and at the same time more characteristic of the molecule than when they are dissolved in water. The addition of water to a solution of cobalt bromide in alcohol was next studied, and an attempt made to show that the change in colour of the solution is due to a balanced action:

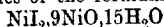


The values of x do, it is true, in most cases approximate to 6, and consequently make it extremely likely that the colour change is brought about by the anhydrous salt changing into the hexahydrate.

J. F. S.

The Absorption of Light by Inorganic Salts. X. ROBERT A. HOUSTON and CHARLES COCHRANE (*Proc. Roy. Soc. Edin.*, 1913, 33, 147—155. Compare preceding abstract.).—The present paper deals with four points arising out of previous papers. (1) Ewan (A., 1895, ii, 433, 471) had pointed out that the molecular-coefficient of copper acetate varied with the wave-length in the same way as the molecular extinction-coefficients of other salts of copper, but its value was approximately two and a-half times the value of the latter. Curves showing the relationship between the sulphates and acetates of copper, nickel, and cobalt are given, which show the abnormality of copper acetate. This is attributed to a difference in chemical constitution. (2) With respect to the colour of ions the authors show that the molecular extinction-coefficient remains constant at low concentrations, and increases asymptotically as saturation is reached. The behaviour is entirely different from that of the molecular conductivity; consequently there is no connexion between the two quantities. The authors draw the conclusion, therefore, that ionisation has nothing whatever to do with the

colour changes of copper, nickel, cobalt and iron salts in solution. (3) It is shown from the shape of the curve for the extinction-coefficient of anhydrous cobalt chloride in acetone that the acetone doubtless combines with the cobalt chloride; and (4) the absorption of cobalt and nickel iodides had been previously shown to have very large absorptions approaching that of iodine. The results were redetermined and shown to vary with the age of the solution. Eventually it is shown that the two iodides break up in solution into iodine and oxyiodides of the formulae $\text{Co}_2\text{I}_3\text{O}$ and



respectively, thus explaining the high absorptive values of the solutions, J. F. S.

The Absorption of Light by Inorganic Salts. XI. Conclusion. ROBERT A. HOUSTON (*Proc. Roy. Soc. Edin.*, 1913, 33, 156—165. Compare preceding abstracts).—A theoretical paper in which the work published in the preceding papers is criticised, together with the various theories of absorption. The author states that there is no spectroscopic evidence in favour of the theory of electrolytic dissociation, but there is some evidence against it which can, however, be surmounted by the assumption of hydrolysis, complex ions, hydration, etc. J. F. S.

Quantitative Investigation of the Absorption of the Ultra-violet Rays by Aliphatic Monamines, Diamines, Nitriles, Carbylamines, Amides, and Oximes. JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1913, 156, 1860—1863).—The authors have studied the influence of the different groups containing nitrogen in the above substances on the absorption of ultraviolet rays, the determinations being made in alcoholic solution. They are led to the following conclusions: (1) In all the cases examined, absorption takes place in a regular manner, the value of the molecular absorption constant increasing with diminishing wave-length of light up to $\lambda = 2144$; (2) absorption of ultraviolet rays by primary amines of the series $\text{C}_n\text{H}_{2n+1}\text{NH}_2$ increases with the value of n . When compared with the corresponding alcohols, the replacement of $-\text{OH}$ by $-\text{NH}_2$ causes a considerable increase in absorption. The absorptive power of the hydroxyl group is small, so that, for the alcohols, the influence of the alkyl group is the predominant factor. The absorption of alcohols of the series $\text{C}_n\text{H}_{2n+1}\text{OH}$ increases with the value of " n " according to an exponential law. On the other hand, the influence of the amino-group in primary amines is very considerable, and masks the absorption due to the alkyl group in such a manner that the relative variations of the absorption with regard to the value of " n " are small; (3) secondary and tertiary amines resemble primary amines in their general behaviour; (4) when the hydrogen atoms in ammonia are successively replaced by alkyl groups of the formula $\text{C}_n\text{H}_{2n+1}$, a strongly marked increase of absorption is noticed which follows an exponential law; thus, for $\lambda = 2389$ the values of ϵ are 0.66 for methylamine, 1.8 for dimethylamine, and 15.8 for trimethylamine; (5) the absorption curve of

ethylenediamine resembles that of ammonia; (6) substances in which nitrogen is triply linked to carbon or is quinquivalent have very little absorptive power; (7) the absorption of amides resembles that of the corresponding acids. Substitution of the hydroxyl by the amino-group produces an increase in absorption, which, however, is of relatively less importance than in the case of alcohols and primary amines, since the absorption due to the acyl group is itself considerable; (8) the absorption of oximes is greater than that of amines, and substitution of the two atoms of hydrogen of the NH_2 group by alkyl radicles produces a very marked increase in absorptive power.

H. W.

Action of Radiations on a Mixture of Coloured Substances. P. A. DANGEARD (*Compt. rend.*, 1913, 156, 1844—1845).—It has been previously shown that only the rays actually absorbed are causative of the decolorisation of chlorophyll. When light is allowed to act on a mixture of chlorophyll and pinaverdol, the latter is first decolorised at the first absorption band of the chlorophyll, later at its own absorption band; in the absence of chlorophyll, pinaverdol is only decolorised at its own absorption band, from which it follows that the latter is attacked and finally destroyed through the energy absorbed by the chlorophyll, and not by that absorbed by itself. The experiments have been extended to a variety of coloured substances, with the general result that radiations which are completely inactive towards a pure substance are found to become active in the presence of a second pigment. Since chlorophyll in the plant is accompanied by various yellow pigments, such as carotene and xanthophyll, and decolorisation is complete at the bands I, II, III. and IV, it follows that these pigments are also attacked and ultimately decomposed through the energy absorbed by the chlorophyll.

H. W.

Colorimetric Dilution Law. ARTHUR HANTZSCH (*Annalen*, 1913, 399, 379—384).—Several examples have been given by the author of substances which attain a state of isomerism-equilibrium in solution and exhibit variations from Beer's Law. It is now stated that these abnormalities are due to the presence of traces of impurities in the solvent or in the solute. Ethyl acetoacetate in very carefully purified hexane follows the law, although in ordinary hexane it exhibits abnormalities. Optical abnormality is shown by the colourless and the yellow modifications of ethyl dichlorodihydroxyterephthalate in all solvents; this is due to an impurity in the solute, because the more easily purified methyl ester obeys Beer's law in all solvents. Doubtless the same explanation accounts for the abnormal optical behaviour of the colourless and the yellow modifications of nitro-*p*-acetotoluidide.

The variations of the chromoisomeric pyridine, quinoline, and acridine salts from the colorimetric dilution law can be explained by the ionic hypothesis in the case of dissociating solvents; a satisfactory explanation of the abnormalities in non-dissociating media cannot be given.

C. S.

Interference Phenomena of Pleochroic Liquid Crystals in Convergent Polarised Light. DANIEL VORLÄNDER and M. E. HUTH (*Zeitsch. physikal. Chem.*, 1913, 83, 723—727).—It is shown from a study of the interference figures of liquid crystals that they are analogous to uniaxial crystal plates cut at right angles to the crystal axis. Mixtures of liquid crystals when examined under crossed nicols do not show the same colours in all four quadrants of the interference figure. This was noticed first with a mixture of *p*-cyanobenzylideneaminocinnamic active amyl ester and *p*-cyanobenzylideneanisidine. This behaviour is found in the case of all strongly pleochroic and circularly polarising liquid crystals. A number of coloured diagrams of interference figures are appended to the paper. J. F. S.

Studies of the Processes Operative in Solutions. XXVIII. The Influence of Acids on the Rotatory Power of Cane Sugar, of Glucose, and of Fructose. FREDERICK P. WORLEY (*Proc. Roy. Soc.*, 1913, A, 88, 439—443).—The author has studied the effect of adding benzenesulphonic acid in different dilutions to solutions of sucrose, dextrose, and laevulose with respect to the rotatory power. It is shown that the large alteration produced by the acid in the value of the ratio of the final to the initial rotation in experiments on the hydrolysis of sucrose can be completely and satisfactorily explained by the changes produced by the acid on the rotatory powers of the three sugars involved. J. F. S.

Energy Changes during Photochemical Reactions in Gases. III. Photochemical Deozoneisation. EMIL WARBURG (*Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 644—659. Compare A., 1911, ii, 834; 1912, ii, 315).—The author has investigated the decomposition of ozone by light of known wave-length. The ozone was mixed with oxygen, nitrogen, and helium respectively. It is shown that the Einstein photochemical equivalent law (*Ann. Physik*, 1912, [iv], 37, 832) holds for the cases examined. It is also shown that the specific photochemical deozoneising is approximately twice as large in moist ozone-oxygen mixtures as in the corresponding dry mixtures. The spontaneous decomposition of ozone is increased by the presence of aqueous vapour. The photochemical action in concentrated ozone-oxygen mixtures decreases with the intensity of the illumination. J. F. S.

Photochemical Decomposition of Solutions of Oxalic Acid in Presence of Uranyl Nitrate. MARCEL BOLL (*Compt. rend.*, 1913, 156, 1891—1894).—It has been shown previously (Fay, A., 1896, i, 464) that oxalic acid is decomposed by uranyl nitrate in presence of light, and that the nitrate is unchanged at the end of the reactions. The author finds that the acid is oxidised to carbon dioxide. Examined by the method already described (this vol., ii, 171, 265) and the change being measured by conductivity determinations, the reaction was found to be unimolecular, and this was confirmed by determinations of the initial velocity of reaction. If

uranyl nitrate takes any part in the reaction, it must therefore be re-formed as quickly as it is decomposed. The coefficient of absorption of light for the mixture is practically the sum of those of the two components, and the energy absorbed is inferior to that required by Einstein's rule (*J. Phys.*, [v], 3, 277). In this and the case examined by Henri and Wurmser (this vol., ii, 121) systems of false equilibrium are concerned, in which a spontaneous reaction proceeds feebly and is accelerated by light. T. A. H.

Photocatalysis. MARC LANDAU (*Compt. rend.*, 1913, 156, 1894—1896. Compare preceding abstract).—The decomposition of oxalic acid by uranium and its compounds has been investigated, and shown not to be parallel with the radioactivity of the substances used. The lightest and heaviest metal of each of six groups of the periodic table (I, II, III, VI, VII, VIII) were also tried in the form of nitrates, and of these only chromium and uranium (group VI) proved to be active, uranium being three times as active as chromium. A mercury lamp was used as the source of light.

T. A. H.

Quantitative Investigation of the Action of Monochromatic Ultra-violet Rays on Amylase. A. CHAUCHARD and M^{me}. CHAUCHARD (*Compt. rend.*, 1913, 156, 1858—1860).—Two methods have been employed in the study of the effect of variation in the wave-length of the ultraviolet light employed on the rate of destruction of amylase. In the first of these, the source of light is the spark passing between cadmium electrodes. The light is filtered by suitable screens and allowed to traverse the solution of amylase, when it is found that the rays $\lambda = 2469, 2300$, and 2195 are more active than those of greater wave-length. In the second series the light from a spark passing between magnesium, cadmium, or zinc poles is resolved by two quartz prisms, and the individual rays are allowed to act on the amylase solution. The amount of decomposition is found to increase as the wave-length of the light employed decreases.

By a comparison of these results with the absorption of the different rays by the amylase solution, the authors are led to the conclusions that: (i) the photochemical action of ultraviolet rays on a solution of amylase is proportional to the absorption of these rays by the solution, and (ii) an amount of radiant energy sufficient to raise the temperature of the solution through only $\frac{1}{4}$ degree is capable of bringing about the destruction of 40% of the amylase.

H. W.

Light-Reactions Observable in the Cardioid Ultramicroscope. WILHELM BILTZ (*Zeitsch. Chem. Ind. Kolloid.*, 1913, 12, 296—299).—The author records a number of reactions which take place in the strong illumination of the cardioid ultramicroscope (compare Siedentopf, A., 1910, ii, 289). It is shown that a drop of a carbon disulphide solution of sulphur precipitates amorphous sulphur in two to five minutes, and that Fehling solution rapidly

changes from blue to green, yellow, and finally red. Sodium nitroprusside quickly shows the presence of rapidly-moving submicrons the nature of which is unknown, but the author considers that they are not substances of the iron cyanide groups, since they are red in colour. A mixture of mercurous chloride and ammonium oxalate on illumination with white or blue light rapidly shows the formation of feathery crystal-aggregates. Dichromated gelatin, malachite-green, and uranin all show rapid formation of submicrons, indicating that a chemical change has been induced by the light.

J. F. S.

Biochemical Catalysis of a Luminescent Oxidation. JULES VILLE and EUGÈNE DERRIEN (*Compt. rend.*, 1913, 156, 2021—2022).—It has been known for some years that the atmospheric oxidation of lophine in solution in alcoholic potassium hydroxide is accompanied by luminescence (Radziszewski, A., 1881, 488). Luminescence in a much more marked degree is observed if the same quantity of lophine in alcoholic solution is treated with a much smaller quantity of sodium hydroxide, some dilute hydrogen peroxide, and a little hæmatin solution. The peroxydase character on which the effect of the hæmatin depends can be also supplied by hæmin or a little diluted blood. A similar luminescence can be observed during oxidation in pyridine solution, but in this case tartaric acid must be present, and the effect is produced only by hæmatin and hæmin.

D. F. T.

The Equivalence of Ionisation and Chemical Action under the Influence of α -Rays. SAMUEL C. LIND (*La Radium*, 1913, 10, 174).—In the previous paper (*ibid.*, 1913, 9, 426) the values given for the total number of ions furnished by the α -particle should have referred to pairs of ions. This correction does not affect the general conclusions, but necessitates a modification in the mechanism proposed for the formation of ozone in that four ions instead of two are required per molecule of ozone.

F. S.

The Passage of β -Rays Through Matter. J. GEDULT VON JUNGENFELD (*Physikal. Zeitsch.*, 1913, 14, 507—514).—Measurements of the absorption-coefficient μ of the β -rays of uranium-X have been made for a number of new materials (iridium, tantalum, antimony, cadmium, rhodium, sulphur, and sodium), and the results are considered from the point of view of Schmidt's theory of absorption. A number of mixtures and compounds were also studied. Comparison is made between the observed and calculated values of $(\mu/D)_0$, the initial value of the absorption-coefficient divided by the density, for alloys of lead and tin, mixtures of powdered metals, the halogen salts of potassium, and the sulphates of the alkaline-earth elements.

F. S.

Some Experiments to Detect β Rays from Radium-A. WALTER MAKOWER and SYDNEY RUSS (*Proc. Physical Soc.*, 1913, 25, 253—255).—Since when an atom of radium-A disintegrates, the

atom of radium-*B* formed carries a single positive charge, and the α -particle expelled carries two positive charges, it must be supposed that three negative electrons are also expelled. Attempts to detect a β -radiation from radium-*A* were made by two methods without success. The curve of the rise of β -rays from pure radium emanation with time, through a thickness of material only just sufficient to absorb the α -rays of radium-*C*, agreed with the theoretical curve calculated on the assumption that radium-*A* gives no β -rays. The magnetic spectrum of the β -rays from a bare wire covered with radium-*A*, by exposing it for five minutes to the emanation, showed only the known β -rays due to radium-*B*. Possibly negative electrons may be expelled as δ -rays which would escape detection by these methods.

F. S.

Origin of Penetrating Rays. VIKTOR F. HESS (*Physikal. Zeitsch.*, 1913, **14**, 610—617).—The author, making use of ionisation experiments at a height of 5350 metres and other controlling experiments (*Physikal. Zeitsch.*, 1912, **13**, 1084), develops a theory of the very penetrating atmospheric rays. It is shown that at a height of above 1000 metres, the penetrating rays operative at the earth's surface are inoperative. The measurements were made by means of a Wulf apparatus, and a formula is developed which gives the quantity of γ -rays emanating from the radium-*C* particles in the air. Special experiments were made with a radium standard, which enables conclusions to be drawn with respect to the quantity of radium-*C* and emanation in the air. The value obtained is between $1.6-1.9 \times 10^{-16}$ Curie per c.c., whereas the quantity present at the earth surface is about 1/20th of this amount. Since the concentration of the emanation in the air cannot be more than that at the surface, it follows that the radium-*C* particles in the air are responsible for only 1/20th of the penetrating rays. Consequently it follows that a very large portion of the penetrating rays are not caused by the known radioactive substances on the earth's surface or in the atmosphere.

J. F. S.

A Cathode-ray Vacuum Furnace. ERICH TIEDT (*Ber.*, 1913, **16**, 2229—2233).—A description of a furnace which is so arranged that the cathode rays fall directly on a crucible containing the substance to be investigated. Full dimensions are given, since it was only with these particular dimensions that success was attained.

Iron, nickel, chromium, platinum, tantalum, boron, etc., were readily melted in the furnace. Calcium carbide was dissociated at the temperatures produced, giving metallic calcium. T. S. P.

Secondary Rays from Canal Rays. HANS BAERWALD (*Ann. Physik.*, 1913, [iv], **41**, 643—669).—Using an aluminium electrode in hydrogen, the author arrives at the following conclusions: (1) That with increasing velocity of the primary rays the velocity of all secondary rays is increased to a definite maximum velocity. (2) The quantity of the secondary radiation is proportional to the intensity of the primary radiation. (3) The velocity of the free secondary

electrons is independent of the intensity of the primary canal rays. (4) The ability of hydrogen canal rays to produce secondary radiation demands a minimum potential of 900 volts. (5) At the highest discharge potentials, 95% of the secondary radiation has a velocity of less than that corresponding with 10 volts. (6) A higher velocity of the primary ray particles corresponds with a higher velocity of the secondary electrons. A series of experiments were made in air and hydrogen with the metals iron, copper, zinc, silver, platinum, gold, and lead, and a further series in hydrogen alone with carbon, magnesium, sulphur, calcium, thallium, bismuth, uranium, and copper oxide, and in this connexion it is shown that the influence of the primary radiation on the velocity distribution of the secondary radiation at a definite discharge potential depends on the atomic weight, and not on the chemical characteristics of the metal, and, further, that the influence of the primary radiation on the quantity of the secondary radiation does not depend on the atomic weight or the chemical character of the metal, but on the number of particles in unit volume composing the ray. The nature of the metal on which the canal rays strike, is without influence on the velocity and quantity of the secondary radiation. J. F. S.

Bending of Rubidium Rays in a Magnetic Field. KARL BERGWITZ (*Physikal. Zeitsch.*, 1913, 14, 655—658).—It is shown that the radiation from rubidium consists of β -rays. The velocity of these rays approximates to 1.85×10^{10} cm. per sec. J. F. S.

Energy Required to Ionise an Atom. R. T. BEATTY (*Phil. Mag.*, 1913, [vi], 26, 183—186).—The author deduces an expression for calculating the energy required to remove an electron from an atom; for helium the expression has the form $Ee = 1.5 \cdot e^2/a$, where E is the energy required, $2e$ is the central positive charge of the helium atom, and a is the radius at the end of which the electrons are situated. Values of E are calculated for helium, neon, and argon, and they are very near the values experimentally determined by Franck and Hertz (this vol., ii, 174). J. F. S.

Ionisation Potential in Gases. R. T. BEATTY (*Physikal. Zeitsch.*, 1913, 14, 622).—The energy required to remove an electron from an atom is worked out by the author. A series of figures denoting the molecular radius and the observed and calculated E.M.F. required to effect the separation of atom and electron in the case of the inactive gases is given. J. F. S.

The Spontaneous Ionisation of the Air in a Closed Vessel. J. J. REY (*Le Radium*, 1913, 10, 137—141).—Contrary to the experience of other workers, but in conformity with those of Patterson (A., 1903, ii, 194), the spontaneous ionisation in a large vessel was found to be nearly proportional to the pressure for pressures below 15 cm. of mercury, and to be nearly independent of the pressure above 30 cm. of mercury. The closed vessel was a cylindrical brass receptacle of 13 litres capacity, thickly coated on the

inside with solder, and giving a production of about 100 ions per c.c. per second. The exact form of the curve connecting ionisation with pressure revealed an ill-defined maximum of ionisation at about 50 cm. of mercury. The curve is easily explained as being formed by the superposition of two radiations, the one very easily absorbed producing most of the ionisation at low pressures and the other very penetrating, producing ionisation small at low pressure, but increasing proportionately to the pressure.

The spontaneous fluctuations of the ionisation current in the chamber, the effect of dust, and of the presence of radium emanation initially in the air were also studied. F. S.

Recombination of Ions Produced by Röntgen Rays in Gases and Vapours. H. THIEKILL (*Proc. Roy. Soc.*, 1913, 88, A, 477—494).

—Experiments are described on the recombination of ions in air, carbon dioxide, carbon monoxide, sulphur dioxide, and nitrous oxide. The measurements were made at 15° under varying conditions of pressure, electric field, and intensity of ionisation. The experiments were rendered uniform by producing the ionisation by means of a single flash from a Röntgen ray bulb. The experiments show that recombination takes place according to the expression $dn/dt = -an^2$ when both ions are present in equal concentrations, or generally $dn_1/dt = -an_1n_2 = -dn_2/dt$, in which n_1 and n_2 represent the number of positive and negative ions respectively, t is the time, and a the coefficient of recombination. The coefficient of recombination varies with the pressure, and throughout a considerable range of pressure is proportional to the pressure. J. F. S.

Measurement of the Valency of Ions in Gases. P. LANGEVIN

(*Le Radium*, 1913, 10, 113—118).—The theory is discussed of a method for determining K/D , the ratio of the mobility to the coefficient of diffusion of gaseous ions, with the object of determining the valency of the ions. The gas between two parallel metal plates, placed very near together, is ionised by an exterior radiation traversing the gas normally to the surface of the plates. The production of ions in the volume of the gas may be considered uniform, provided that the distance between the plates is of the same order as the average path of the secondary rays in the gas, which is fulfilled even in the case of X-rays when the thickness of the gaseous layer is of the order of a millimetre. In these conditions the permanent regime which establishes itself between the plates is determined, in the first place, by the loss of ions by diffusion rather than by recombination, and the quotients K/D and K'/D' for positive and negative ions can be determined by following the variation of current with the difference of potential established between the plates. Expressions for the variation of current with potential are worked out to the first and second degree of approximation, and obtained in a form such as to admit of the experimental determination of the valency of the ions. F. S.

Researches on the Valency of Ions in Gases. EDOUARD SALLÉS (*Le Radium*, 1913, 10, 119—122).—Langevin's method of

determining K/D has been put into practice, using the β -rays of 7 mg. of a radium salt. The comparison of the curves obtained, representing current and voltage, with those theoretically to be expected for the case of univalent ions, for thicknesses of air ranging from 2.7 to 0.3 mm., gave values for K/D , for different portions of the curve, from 1.0 to 1.23×10^4 , whereas, if any ions of higher valency had been present, the effect would have been to increase the value beyond 1.23×10^4 , the value theoretically to be expected for univalent ions. The results bear out those of Millikan and of Franck and Westphal.

F. S.

The Magnetic Separation of Ions Emitted by the Spark in a Rarefied Gas. AUGUSTO RIGHI (*Le Radium*, 1913, 10, 134—136).—At one end of a tube are two electrodes connected with an influence machine, furnishing about 0.3 milliamperes, two condensers of capacity about 37,620 *E.S.U.*, and a spark-gap of from 2 to 4 mm. between brass balls 5 cm. diameter. The tube is exhausted to 0.04 mm. pressure, and a magnetic field established across it to deviate the positive and negative ions produced by the spark in the tube to two electrodes suitably placed. Under these circumstances, a current passes between the electrodes, reaching a maximum of about 30 micro-amperes as the strength of the magnetic field is increased. The effect is somewhat analogous to the Hall effect, the rarefied gas replacing the metallic plate. Using an induction coil instead of an influence machine, the current may be increased ten or twenty times, and an ordinary galvanometer of medium sensitiveness used to demonstrate them.

F. S.

The Ionisation of Liquid Dielectrics by the Radium Emanation. GEORGE JAFFÉ (*Le Radium*, 1913, 10, 126—134. Compare Abstr., 1910, ii, 481).—The ionisation produced by the emanation of radium in carefully purified hexane, carbon tetrachloride, and carbon disulphide has been studied in a glass condenser. An unknown quantity of emanation was introduced into the liquid, and the current for various potentials measured; an unknown fraction of the emanation was withdrawn by an air stream, and its quantity measured in an air condenser; the current in the liquid was again measured, and the difference between the two currents thus found for a known quantity of emanation. The currents so observed were very small, and for the α -rays were only of the order of one thousandth of that produced by the emanation in air. The effects due to the α - and β -rays of the several products were separated, and the effects due to the β -rays were of the order of one tenth of that produced in air. Tables are given showing the number of ions produced per second per curie in the three liquids by the α -rays of radium-A and radium-C, and by the β -rays of radium-B and radium-C. The results are compared mathematically, and shown to be in agreement with what is to be expected from the theory of columnar ionisation applied to liquids. The only essential difference between ionisation in liquids and in gases is regarded as being that in the former only an insignificant fraction of the ions formed

escape recombination in the columns in which they are produced, but this part, in spite of the great density of the ions in the columns in liquids, obeys the same laws of mobility, recombination, and diffusion as are valid for ions in gases. F. S.

The Fractional Adsorption of Radium-Barium Salts, and the Fractional Electro-dialysis of the Adsorption Compounds thus Obtained. EATON EBLER (*Eighth Inter. Cong. App. Chem.*, 1912, 2, 91--93).—An extension of the method previously described (A., 1911, ii, 957) to other colloids indicates that they do not all show a like selective adsorption towards radium salts, and also that the adsorption depends on the nature of the radium salt used. Of the colloids investigated, manganese dioxide hydrate shows marked adsorptive power for nearly all radium salts; basic ferric carbonate acts similarly towards radium carbonate, so that when a solution containing radium salts and an excess of ferric salt is precipitated with sodium carbonate, all the radium is carried down with the iron precipitate. If this precipitate is then dissolved in the necessary amount of dilute hydrochloric acid to give the colloidal sol, $\text{Fe}(\text{OH})_2\text{Cl}$, and the sol dialysed, the radium salts can be separated; barium salts, if present, pass through the dialyser at a different rate from the radium salts, and thus fractionation can be brought about. The dialysis can be accelerated, in an obvious manner, by electrolysis, the phenomenon of electro-cataphoresis often aiding the process.

The adsorption compounds with manganese dioxide and silicic acid gels may be submitted directly to dialysis or electrodialysis, without being first brought into the sol condition. T. S. P.

The Solubility of the Active Deposit of Radium. EVA RAMSTEDT (*Le Radium*, 1913, 10, 159—165).—Plates were exposed to dried radium emanation overnight, without application of an electric field, and the activity two hours after removal compared with that remaining after treating a certain time with a solvent. From the curves the loss of activity of both radium-B and -C could be separately deduced. Glass surfaces give better and more regular results than those of gold and platinum. Only about one-half (mean 0.52) of the active deposit on a glass surface is readily dissolved; the other half is not dissolved at all on boiling with acid, but with gold and platinum the soluble part amounts to 60—70%. This is explained by the recoil of the radium-B particle in its formation from radium-A, driving it into the surface. For radium-B deposited on a plate by projection from a radium-A surface the whole is soluble.

The measurements of solubility were carried out with two similar plates, one of which was subjected to standard treatment, the same in all cases. Radium-C is soluble in the common acids, less so in alkaline liquids and in water, and very little in organic solvents. Radium-B dissolves more quickly than radium-C in water and acids, especially when dilute, less quickly in alkaline liquids, and very little in organic solvents. Radium-A is more soluble than

radium-*B* and -*C*, and dissolves even in organic solvents, especially carbon disulphide, which confirms its position in the sulphur family of elements. The speed of solution increases with the temperature of the solvent, and Arrhenius's formula applies approximately. It was found by depositing the active material on plates of gold and platinum previously saturated electrolytically with hydrogen and oxygen that oxygen enormously diminishes the solubility, especially of radium-*C*, whilst hydrogen diminishes the relative speed of solution of radium-*A*. The influence of oxygen on solubility is analogous to that on volatility.

F. S.

Position of the Radioactive Elements in the Periodic System. KASIMIR FAJANS (*Le Radium*, 1913, 10, 171—174).—Owing to the discovery of a short-lived product of uranium-*X*, called uranium-*X₂* (Fajans and Göhring, *Naturwissenschaften*, 1913, 1, 339) of half period 1·1 minutes, the only remaining possibility as regards the origin of actinium is that it comes from a β -ray change of radium, and the atomic weight of actinium will then be equal to that of radium. On this assumption, the following generalisation holds. The α -ray-giving members of a non-separable group of elements have longer periods of life according as their atomic weight is higher. For the β -ray-giving members the reverse is the case. For the α -ray rule radium-*F* is an exception. For the β -ray rule actinium-*B* and -*X* are exceptions. This point of view explains the small content of lead in thorium minerals, free from uranium, because the end-product of thorium in the lead place in the periodic table, with atomic weight 208·4, ought to have a shorter period of life than radium-*G* (lead), atomic weight 206·5, although longer than that of radium-*D*, atomic weight 210·5.

F. S.

Activity of Subsoil and Atmospheric Air in November and December, 1912. JOSÉ MUÑOZ DEL CASTILLO and JOSÉ BARRIO FERNÁNDEZ (*Anal. Quim. Fis.*, 1913, 11, 294—307).—It is suggested that probably the activity of the sub-soil may be related to the pressure and temperature, but it is not influenced by the wind. Up to 0·5 metre depth the activity of the air and of the sub-soil appear to be related. Below 2 metres this activity increases with the depth, and the activity is greater in firm than in loose soil.

G. D. L.

Relation between the Limiting Values of the Molecular Conductivity and Internal Friction in Non-aqueous and Aqueous Solutions. PAUL WALDEN (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 559—582).—In order to investigate the extent to which the law $\lambda_{\infty} \cdot \eta_{\infty} = \text{constant}$ (see A., 1906, ii, 335; 1912, ii, 23) is applicable, the author has examined the following cases.

(1) Tetramethylammonium iodide in benzyl cyanide. (2) Tetramethylammonium iodide in methyl and ethyl alcohols, acetonitrile, ethyl cyanoacetate, and acetone; with ethyl alcohol, $\lambda_{\infty} \cdot \eta_{\infty} = 0\cdot524$, whilst with the other four solvents the values lie within the limits 0·562 and 0·567. These results show that, in the solvents

employed, the above salt containing the complex cation, $N(C_5H_{11})_4$, behaves in exactly the same way as potassium iodide, only the absolute value of the product changing from salt to salt; thus, the four homologous tetralkylammonium iodides give the values: methyl, 0.745; ethyl, 0.700; propyl, 0.624; amyl, 0.557. It is found also that, if V is the molecular volume of a large ion, the law $\lambda_\infty \cdot \eta_\infty \cdot \sqrt[3]{V} = \text{const.}$ holds for different salts of a homologous series, independently of the solvent (see Herzog, A., 1911, ii, 23).

(3) Piperidine picrate in water, propionitrile, acetone, furfuraldehyde, ethyl cyanoacetate, nitromethane, acetylacetone, benzonitrile, methyl thiocyanate, methyl and ethyl alcohols and acetonitrile. With all these solvents except ethyl alcohol, the differences from the mean value of 0.632 are less than $\pm 2\%$. Although fundamentally different in their chemical relations, piperidine picrate and tetrapropylammonium iodide differ little in molecular weight, number of atoms in the molecule, and value of the product $\lambda_\infty \cdot \eta_\infty$; the conclusion is therefore drawn that, also with organic solvents, the sum of the velocities of migration or the molecular conductivity depends principally on the number of atoms composing the salt.

(4) Triamylamine picrate in ethyl and methyl alcohols, water, ethyl cyanoacetate, acetonitrile, and nitrobenzene. In this case $\lambda_\infty \cdot \eta_\infty = 0.509 \pm 0.005$, the values for tetra-amylammonium iodide and sodium iodide being 0.557 and 0.556 respectively. The fact that the simple cation, Na^+ , exhibits the same velocity of migration as the complex one, $N(C_5H_{11})_4^+$, is understandable only if the former is surrounded by an extensive atmosphere of molecules of the solvent.

(5) The values of $\lambda_\infty \cdot \eta_\infty$ for tetramethylammonium nitrate in acetonitrile (0.759), methyl alcohol (0.753), nitromethane (0.774), and ethyl cyanoacetate (0.758), and (6) those for tetramethylammonium thiocyanate in acetone (0.755), acetonitrile (0.769), methyl alcohol (0.770), and ethyl cyanoacetate (0.775) are given in brackets.

Hence, if the value of the product $\lambda_\infty \cdot \eta_\infty$ for a given salt in an efficient and readily accessible solvent of considerable ionising power is known, the value of the limiting molecular conductivity for the same salt in a second solvent can be calculated from the expression:

$$\lambda^1_\infty = \lambda_\infty \cdot \eta_\infty / \eta^1_\infty = \text{const.} / \eta^1_\infty.$$

Such a method of calculating is of value in determining the degree of dissociation at any dilution, $r(\gamma = \lambda^1_r / \lambda^1_\infty)$, either of slightly dissociated salts or of good electrolytes in solvents of low ionising power.

T. H. P.

Electrical Emissivity and Disintegration of Hot Metals.
JOHN A. HARKER and GEORGE W. C. KAYE (*Proc. Roy. Soc.*, 1913, **4**, 88, 522—538. Compare A., 1912, ii, 525).—The authors describe experiments on the metals platinum, iridium, iron, tantalum, copper, nickel, and brass. The metals were heated by an alternating current, and no potential was applied; the experiments were carried out in

nitrogen at low pressures. It is shown that the emission of positive electricity occurs at temperatures from 1000° to 1400° . For metals which melt within this range, a sudden and marked increase in the positive current often occurred at the melting point, due probably to a sudden release of occluded gas. The presence of oxygen augments the positive current. At higher temperatures negative electricity predominates, and increases rapidly with the temperature. The negative current attained with iridium at the melting point was 80 milliamps., with tantalum at 1670° , 220 microamps., with iron at the melting point, 90 microamps. In the case of carbon in air at 760 mm. an ionisation current of $3\frac{1}{2}$ amps. was obtained. The negative current at moderate pressures appears to be largely increased if the conditions are such that considerable "sputtering" of the metal occurs. The negative currents are probably a consequence of chemical action between the metal and the surrounding gas. Carbon becomes plastic in the neighbourhood of 2500° , and readily sublimates at the same temperature.

J. F. S.

New Processes for the Production of Electricity which Explain Some Bioelectrical Phenomena. II. REINHARD BEUTNER (*Zeitsch. Elektrochem.*, 1913, 19, 467—477. Compare this vol., ii, 468).—A continuation of the work published in part I (*loc. cit.*). Experiments are described which show that at the surface of salicylaldehyde and aqueous salt solutions, potential differences exist which vary reversibly with the concentration in the same way, no matter which salt is in the aqueous solution. This is as was to be expected from the theory deduced previously (*loc. cit.*). Equally concentrated solutions of different cations give large, although different, potential differences. It is shown how the potential difference of cells containing several such single potential differences may be calculated from thermodynamical considerations. It is shown that both the strength and concentration of the acid in the non-aqueous phase influence the dimensions of the potential variations with concentration change. The addition of non-electrolytes, such as sugar, which are soluble only in the aqueous phase, do not affect the potential difference, but the addition of substances like alcohol and ether, which are soluble in both phases, and thereby change the distribution-coefficient of the salts, cause a change in the potential difference, and this is the same as that observed for plant membranes. Finally, measurements were carried out with basic substances insoluble in water; these substances give rise to *E.M.F.*'s which change in the opposite direction to that observed for acidic substances, that is, there is a reversibility for the anion. The *E.M.F.* in these cases is analogous to the *E.M.F.* obtained for acidic substances, and can be treated by the mathematical expressions given in the earlier paper (*loc. cit.*).

J. F. S.

[Measurement of Polarisation Potential.] DAVID REICHENSTEIN (*Zeitsch. Elektrochem.*, 1913, 19, 518—520).—The author shows that in his measurements on polarisation potentials (A., 1912, ii, 1037) an error was introduced by measuring this with a hydrogen elec

trode. The value thus obtained gave the sum of two potentials, namely, that of the polarisation and that of the polarising-current. It is shown that by using the Haber-Luggins capillary method quite different values are obtained, and these represent the true values.

J. F. S.

Theory of Chemical Polarisation of Reversible Electrodes. Anodic Behaviour of Mercury, Copper, and Silver Copper Alloys. DAVID REICHNSTEIN (*Zeitsch. Elektrochem.*, 1913, 19, 520—530. Compare preceding abstract).—The author puts forward an hypothesis which considers the positive and negative polarisations as similar and comparable processes. The reasons for the deposition of alloys on the cathode in electrolysis are developed, and the solution of an anode alloy is treated as a special case of negative depolarisation. The second part of the paper is experimental, and deals with the polarisation of the electrodes $\text{Cu}|\text{CuSO}_4$, $\text{CuHg}|\text{CuSO}_4$, and $\text{CuAg}|\text{CuSO}_4$, in the presence of sulphuric acid of various concentrations. The current density potential curve and the time potential curves of these elements are determined.

J. F. S.

Influence of the Addition of Free Sulphuric Acid and its Neutral Salts on the Cathodic Polarisation of the $\text{Cu}|\text{CuSO}_4$ Electrode. DAVID REICHNSTEIN and A. ZIEREN (*Zeitsch. Elektrochem.*, 1913, 19, 530—534. Compare preceding abstracts).—It is shown that the cathodic polarisation of a $\text{Cu}|\text{CuSO}_4$ electrode gives an entirely different current density potential curve when a measurable quantity of hydrogen ions are present. The addition of free sulphuric acid or neutral sulphates [K_2SO_4 , MgSO_4 , ZnSO_4 , Na_2SO_4 , and $(\text{NH}_4)_2\text{SO}_4$] brings about a considerable increase in the polarisation. The nature of the current-density concentration curve leads to the conclusion that the addition of the sulphates brings about a decrease of the Cu^{++} ion concentration in the electrolyte, and the slow reaction, on which the chemical polarisation depends, consists in the reduction of the Cu^{++} ions by a cathodically produced reducing agent, and not in the slow production of Cu^{+} ions from the undissociated copper sulphate in the solution.

J. F. S.

Minimum Potential of Electrolytic Valves in the [Direction of the Current]. GÜNTHER SCHULZE (*Ann. Physik*, 1913, 41, [iv], 593—608. Compare A., 1907, ii, 842; 1908, ii, 350, 560, 658; 1909, ii, 371).—Electrolytic valves are shown to prevent the passage of current in the direction of flow as long as the applied potential does not reach a given minimum value. The size of the minimum potential depends on the metal of which the valve is made, the thickness of the gas layer on the metal, and the nature of the electrolyte. The minimum potential of tantalum is 1.51 times that of aluminium when both metals have been prepared at the same potential. The minimum potential increases slightly with the preparation potential and the thickness of the active layer. The minimum potential increases about 7% when the ionic concentration

of the electrolyte is decreased by one-half. In 0.2*N*-solutions of nitrates, after preparation of the valves by a direct current of 85 volts, the minimum potential of tantalum for alkali cations is about 10 volts, and for most other cations about 30 volts. The minimum potential for H ions is particularly high, 46.3 volts. Of the anions the aluminate anion AlO_2^- has an abnormally low minimum potential, 4.3 volts, and the Cl^- and NO_3^- ions relatively high values, namely, 18.2 and 11.7 volts for 0.05*N*-solutions of the sodium salts. Tables of values for a large number of anions and cations, with and without addition of other substances, are given in the paper. J. F. S.

Normal and Liquid Potentials in Non-aqueous Solutions. Correction. N. ISGARISHEV (*Zeitsch. Elektrochem.*, 1913, 19, 491).—Correction to the author's paper (A., 1912, ii, 729). The value of E_a for silver in methyl-alcoholic solution is shown to be 0.9100 volts instead of the lower figure published previously. J. F. S.

Electrocapillary Phenomena at the Surface [of Contact] of Immiscible Liquids. P. KANDIDOV (*Zeitsch. physikal. Chem.*, 1913, 83, 587—591).—The author has determined the relationship which exists between the capillarity of two liquids to which definite but variable potentials are applied. The apparatus is a modified Lippmann electrometer, having three limbs; this contains one of the liquids; the other is contained in a capillary tube which dips into the central limb. Electrodes are introduced into the two liquids so that they are as near as is possible to the surface of separation. The liquids used in the experiments were ether and a 5% solution of uranium nitrate in water. The potentials applied varied from 1 to 20 volts. It is shown that with increasing potential difference the surface tension increases to what is apparently a limiting value at about 12 volts. J. F. S.

Passivity of Metals and its Dependence on the Solvent. N. ISGARISHEV (*Zeitsch. Elektrochem.*, 1913, 19, 491—498).—The author has studied the conditions under which the metals nickel, cobalt, iron, cadmium, copper, and zinc become passive in alcohol solutions and also in water solutions. The process is followed by means of *E.M.F.* measurements. The *E.M.F.* of nickel against a solution of nickel chloride in alcohol was measured, and the value found to increase rapidly, that is, the metal became passive; on removing the metal and cleaning it, it showed its original potential on again immersing in the liquid, but became passive much more rapidly than before, and on repeating the process the rate at which it became passive continued to increase. A fresh piece of nickel dipped in the solution which had been used became passive very rapidly. A solution of nickel chloride in alcohol was left for two days in contact with a piece of nickel; on using this solution for the *E.M.F.* measurements, it was shown that the nickel became passive very rapidly. If all oxygen was removed from the solution and the measurements were made in a current of hydrogen, the

E.M.F. was constant, and consequently the metal showed no signs of becoming passive; thus it is shown that the passivity of nickel in solution is due to the presence of a soluble substance of the nature of a peroxide, and the main cause of the passivity of nickel in alcoholic solution is the formation of an oxide coating on the metal. Similar results were arrived at for cobalt, iron and cadmium. In the case of copper in cupric chloride solution it is shown that the presence of a complex compound of alcohol and cuprous chloride, $\text{Cu}(\text{C}_2\text{H}_5\text{O})_2 \cdot \text{CuCl}_2$, conditions the passivity of copper. Hypotheses concerning the action of this complex in the case of copper passivity are considered.

J. F. S.

Acid and Base as Expressions of the Intensity of Electrons

ERNST CRATO (*Ber. D-ut. pharm. Ges.*, 1913, **23**, 331—355).—A theoretical paper, in which the author seeks to show that acidity is not a chemical property of H ions, but a physical property of all anions, and probably an expression of the intensity of the electrons in the anions, basicity in the same way being an expression of the intensity of electrons in cations. The intensity depends on the nature of the substance, and is probably the source of energy in electrolytic dissociation and in the chemical action of ions. Some reactions which are anomalous when viewed from the point of view of the ordinary electrolytic dissociation theory, are described and discussed on the new basis.

T. A. H.

Electrolysis of Solutions of Lithium Hydroxide. WILLIAM

RECHNER DE CONINCK and A. BOUTARIC (*Ann. Chim. Phys.*, 1913, [viii], **29**, 471—472).—It has been previously observed by Duter (*Compt. rend.*, 1887, **104**, 354) that the volume of oxygen obtained during the electrolysis of solutions of potassium, sodium, barium, and calcium hydroxides is sensibly less than one half of that of the hydrogen evolved. These observations have been confirmed by Berson and Destrem (*A.*, 1888, 1907). The authors have therefore electrolysed solutions of lithium hydroxide, the cathode being a platinum wire and the anode a platinum plate. The volume of hydrogen liberated is always more than double that of the oxygen, varying from 2.30 for low-current densities to 2.06 for higher current densities. The phenomenon is not dependent on an absorption of oxygen at the anode, since it does not show an appreciable variation if the latter has been previously used or recently heated. Hydrogen peroxide could not be detected in the liquid surrounding the anode, nor does a peroxide of lithium appear to be formed.

H. W.

The Electrolysis of Silver Nitrite and the Transport Number of the Nitrite Ion. NILRATAN DHAR and DEVENDRA NATH BHATTACHARYA (*Zeitsch. anorg. Chem.*, 1913, **82**, 141—144).

—Silver nitrite has been electrolysed, using a platinum cathode and silver anode. The transport number found for the nitrite ion is 0.539 in 0.01—0.017*N*-solution, and 0.519 in 0.002*N*-solution at 25°. Vogel (*A.*, 1903, ii, 591) found 0.5877 from a 0.05*N*-solution of barium nitrite.

C. H. D.

Concentration Changes in the Electrolysis of Copper Sulphate Solutions. CHARLES W. BENNETT and C. O. BROWN (*J. Physical Chem.*, 1913, 17, 373—385. Compare A., 1912, ii, 646).

—The anode-cathode potential in a cell with a rotating cathode depositing copper increases regularly with the speed of rotation of the cathode. By means of Sand's auxiliary electrode it was found that the solution pressure of the copper cathode increases by upwards of 0.014 volt when the speed of the cathode is increased.

Fine-grained copper produced by electrolysis or by mechanical treatment has a higher solution potential than cast copper. The *E.M.F.* of the cell cast copper | copper sulphate solution | electrolytic copper is 0.006 volt, which is increased to 0.014 volt with rapid stirring. The increase in solution pressure of the rotating cathode during electrolysis is attributed, however, to the increased rate of removal of cuprous salt (ions) with the more efficient stirring, as no such increase occurs when the electrolyte is dilute sulphuric acid free from copper.

The increase in back *E.M.F.* at the cathode does not explain the whole of the increase in the anode-cathode potential, part of which must be attributed to an increased resistance due to air bubbles being drawn down into the solution when the speed of rotation is high.

The variations in anode-cathode potential and cathode solution potential with variations in temperature and in concentration of acid and copper salt and the influence of alcohol are in harmony with the authors' hypothesis. The back *E.M.F.* in acid cuprous chloride solution, however, falls with increased cathode speed. This is attributed to a more rapid removal of the cupric ions from the vicinity of the cathode, but it is not explained why they should tend to collect there.

The solution potential of a rotating copper electrode in nitric acid diminishes with increased speed of rotation owing to the more rapid removal of the active film of nitrous acid (compare Stansbie, *Proc. Faraday Soc.*, November, 1912).

R. J. C.

Photoelectric Phenomenon Shown by Liquid Sulphur Dioxide. JACQUES CARVALLO (*Compt. rend.*, 1913, 156, 1882—1884).

—It has been shown already (A., 1910, ii, 1026) that when a current is passed between platinum electrodes in liquid sulphur dioxide in the dark, the current-intensity falls to a constant minimum. If at this stage the liquid is alternately illuminated and darkened, the current intensity rises to a greater extent at each successive illumination, reaching a maximum at the seventh. and falls at each extinction of the light, the limit of the fall being higher at each successive extinction. These changes are shown by a curve in the original. After the final extinction the current gradually falls to the original minimum.

These two effects occur in the mass of the liquid, and are produced by ultraviolet rays. The positive effect is chemical, and is due to the change represented by the equation $3\text{SO}_2 = \text{S} + 2\text{SO}_3$; the negative effect, which takes place in the dark, is due to the removal of

the impurities by the current. This negative effect is not exhibited when an alternating current is used.

T. A. H.

Thermoelectric Power of Silicon. JOHANN G. KOENIGSBERGER (*Physikal. Zetsch.*, 1913, 14, 658—659).—The author has examined specimens of silicon which have both negative and positive values for the thermoelectric power when in contact with copper. It is shown that this property increases in both cases with the iron content of the silicon. It is determined by the number of electrons on the silicon, and the number of electrons determines the absolute dimensions of the Hall effect, the conductivity, the thermoelectric power, and the Peltier heat effect.

J. F. S.

Magnetic Properties of the Alloys of Iron, Cobalt, Nickel, and Manganese with Boron. ARMAND BINET DU JASSONNEUX (*English Inter. Cong. App. Chem.*, 1912, 2, 165—170).—Measurement of the magnetic permeability of the various alloys of iron with boron (compare A., 1909, ii, 569) shows that it attains a maximum when the composition corresponds with that of the boride, Fe_2B . Similar series of measurements could not be made with alloys of nickel and cobalt, owing to the small quantities of them available, but the few results obtained indicated that the magnetic permeability of nickel is diminished by alloying with boron, at all events at the ordinary temperature; the boride Ni_2B is not attracted even by a strong magnet.

Of the manganese borides, MnB and MnB_2 , only the former possesses magnetic properties other than those possessed by manganese itself. The permeability of the various alloys reaches a maximum at 13—15% of boron.

Hysteresis measurements showed that the various alloys of iron and manganese with boron, as also the borides Fe_2B , MnB , MnB_2 , and CoB , gives flatter cycles than soft iron filings.

Iron boride, Fe_2B , becomes non-magnetic at 740° ; with falling temperature, it becomes magnetic at 730° . Both the borides of iron and cobalt lose their magnetism at a lower temperature than the respective metals.

T. S. P.

Additive Character of Physical Properties in Organo-metallic Compounds. PAUL PASCAL (*Compt. rend.*, 1913, 156, 1904—1906).—It has been shown previously (this vol., ii, 182) that in the case of organo-metallic compounds of the aliphatic series the conservation of diamagnetic properties follows a limit law, but that there are anomalies in the case of aromatic organo-metallic compounds. These anomalies have now been investigated by the determination of the density, refractive index, and coefficient of magnetisation for a number of compounds of both types. Lists of the values obtained are given in the original.

In general, there is an exaltation of the optical properties of the metal (or corresponding multivalent element) in the case of the aromatic compounds and a lowering of the coefficient of magnetisa-

tion. There is therefore no generally additive character in the physical properties in the case of organo-metallic compounds. They may be exceptional in this respect, but the existence of these anomalies indicates that the additive character of physical constants in purely organic substances may be due, not only to the relative independence of the constituent atoms, but also to their low atomic weights and to the constant character of the valencies concerned.

T. A. H.

The Thermo-electricity of Steel. WITOLD BRONIEWSKI (*Compt. rend.*, 1913, 156, 1983—1985).—The author has extended his previous work (this vol., ii, 288) to steels containing respectively 0.07, 0.24, 0.44, 0.79, and 1.12% of carbon; manganese, silicon, sulphur, and phosphorus were also present. The results show that the various critical points and points of recalescence are as readily determined by this method as by any other.

Formulae are given which represent the thermo-electric power of the different steels over a range of temperature between 0° and 700°.

T. S. P.

Relation between the Law of the Compressibility of Gases and the Coefficients of Dilatation. THADDÉE PECZALSKI (*Compt. rend.*, 1913, 156, 1884—1886).—A mathematical paper in which it is shown that the values of p_v for hydrogen, nitrogen, and air, calculated from a knowledge of the values of α and β , the coefficients of dilatation at constant pressure and at constant volume respectively, are in good agreement with the experimental values found by Amagat and Witkowski.

T. A. H.

The Adiabatic Expansion of Liquids. L. GAY (*Compt. rend.*, 1913, 156, 1978—1979).—Using the method previously described (this vol., ii, 382) the author has determined, at different temperatures, the coefficient of adiabatic compressibility of the following liquids: ethyl bromide, isopentane, cyclohexane, carbon disulphide, toluene, carbon tetrachloride, chloroform, and ethyl acetate. From the results obtained the coefficient of isothermal compressibility has been calculated, and found to be in agreement with the results of other observers.

T. S. P.

The Equilibrium Diagram of Both Modifications of Sulphur. WALTHER NERNST (*Zeitsch. physikal. Chem.*, 1913, 83, 546—550).—A theoretical paper in which it is shown that there is no reason for attributing a value other than zero to the integration constant C of the expression of the second law of thermodynamics as applied to the maximum work of condensed systems, namely,

$$A = -T_0 \int^T U/T^2 \cdot dT + CT.$$

Kruly's paper (this vol., ii, 132) is criticised, and an answer given to his method of using the Nernst theorem for calculating the transition point of sulphur (see also Smits, this vol., ii, 499).

J. F. S.

Determination of Specific Heats at Low Temperatures and their Use in the Calculation of Electromotive Force. II. FRANZ POLLITZER (*Zeitsch. Elektrochem.*, 1913, 19, 513—518. Compare A., 1911, ii, 180).—The author has determined the specific heats of mercury, heptahydrated zinc sulphate, mercurous sulphate, mercurous chloride, thallous chloride, and ice at temperatures from the boiling point of hydrogen to about -100° . The values were used to calculate the atomic and molecular heats of the substances, and figures obtained which agree well with those obtained by means of the Nernst-Lindemann-Einstein formula. By means of the specific heats found the author calculates the *E.M.F.* of the elements, $\text{Hg}|\text{HgCl}|\text{PbCl}_2|\text{Pb}$, $\text{Hg}|\text{HgCl}|\text{AgCl}|\text{Ag}$, and $\text{Pb}|\text{PbCl}_2|\text{AgCl}|\text{Ag}$,

making use of the Nernst heat theory. The calculated values agree well with the best experimentally determined values. J. F. S.

Melting Points, Specific Heats, and Heats of Fusion of the Alkali Metals. ÉTIENNE RENGADÉ (*Compt. rend.*, 1913, 156, 1897—1899).—A short description is given of the methods used in purifying the metals, and in determining the constants. The following results were obtained:

Sodium.—Specific heat (solid) $0.2811 + 0.000233t$; (liquid) 0.330 at 98° ; heat of fusion 27.21 ; m. p. 97.9° ; L/T (ratio of atomic heat of fusion to absolute m. p.) 1.69 .

Potassium.—Specific heat (solid) $0.1728 + 0.000142t$; (liquid) $0.1422 + 0.000668t$; heat of fusion 14.67 ; m. p. 63.5° ; L/T 1.70 .

Rubidium.—Specific heat (solid) $0.0802 + 0.000153t$; (liquid) $0.0921 + 0.000026t$; heat of fusion 6.144 ; m. p. 39.0° ; L/T 1.68 .

Cæsium.—Specific heat (solid) $0.0522 + 0.000137t$; (liquid) $0.0604 + 0.000034t$; heat of fusion 3.766 ; m. p. 28.45° ; L/T 1.66 .

T. A. H.

Cryoscopy in Molten Hydrated Salts. CH. LEENHARDT and A. BOUTARIC (*Bull. Soc. chim.*, 1913, [iv], 13, 651—657).—An elaboration of work already published on the cryoscopy of the fused pentahydrate of sodium thiosulphate (compare A., 1912, ii, 234) and an extension of the study to the decahydrate of sodium sulphate. For the latter the latent heat of fusion at 31.3° is found to be 56.9 , which gives $K = 33.5$ in van't Hoff's formula, a value which agrees well with the experimental figure.

W. G.

Lowering of the Freezing Points of Reacting Solvents. PETRUS H. J. HOENEN (*Zeitsch. physikal. Chem.*, 1913, 83, 513—545. Compare this vol., ii, 394).—A theoretical mathematical paper containing a continuation of the author's calculations (*loc. cit.*) applied especially to freezing-point lowerings. It is shown that the freezing point of a salt (acting as solvent) is only lowered by the unlike portion of an added salt containing one ion the same as the solvent; for example, the lowering of the freezing point of potassium chloride is brought about by the SO_4 ion on the addition of potassium sulphate. The dissociation of dissolved salts is not

complete, or is it zero. Only when the ionisation of the solvent is very small can the dissolved substance at very great dilution be completely dissociated, and only under these conditions can the unlike ions lower the freezing point. The rule, "that only the unlike ions lower the freezing point of a primary system," is evolved mathematically for a solvent of any complexity. It is also shown that this rule is a special case of a general law, concerning the lowering of an $(n+1)$ phase-point in a system of n components. This is fully worked out in the paper. The theoretical points evolved in the paper are illustrated, and proved by a consideration of the freezing-point lowerings of potassium chloride, sodium chloride, potassium fluoride, sodium fluoride, potassium nitrate, sodium chlorate, barium chloride, strontium chloride, calcium chloride, and formic acid, by the addition of salts containing one or other of the ions of the solvent, and by the addition of salts containing ions which are both dissimilar. The change in the transition point of Glauber's salt by the addition of various substances (Löwenherz, A., 1896, ii, 149) is considered, and shown to be in accord with the theory evolved. J. F. S.

Vapour Pressure of Metals. H. VON WARTENBERG (*Zeitsch. Elektrochem.*, 1913, 19, 482-489).—The author has determined the vapour pressure of lead, silver, thallium, platinum, and copper by the method previously used by him for the determination of the vapour pressure of silicon (A., 1912, ii, 1137; this vol., ii, 47). The following values were obtained: Lead, vapour pressure (p) at $808^\circ = 1.05 \times 10^{-4}$ atm., $996^\circ = 2.30 \times 10^{-3}$ atm., and $1178^\circ = 2.20 \times 10^{-2}$ atm. The boiling point (b) and the heat of vaporisation (λ) were calculated in each case, $\lambda = 44,000$ cal. and $b = 1630^\circ \pm 20^\circ$. For silver, p at $1178^\circ = 1.90 \times 10^{-4}$ atm., $1316^\circ = 1.08 \times 10^{-3}$; $1435^\circ = 5.10 \times 10^{-3}$; $\lambda = 60800$ cal., $b = 2100^\circ$. For thallium, p at $634^\circ = 7.40 \times 10^{-5}$; $783^\circ = 1.75 \times 10^{-3}$; $970^\circ = 3.20 \times 10^{-2}$; $\lambda = 3800$ and $b = 1306^\circ$. Platinum and copper showed no loss in weight when heated at 1360° . Hence their vapour pressure at this temperature was less than 10^{-5} atm.; tin, however, gave a notable pressure at this temperature, and preliminary experiments are recorded. J. F. S.

Vapour Pressure of Binary Mixtures. JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1913, 83, 599-608).—Polemical against Dolezalek (this vol., ii, 481). The author takes exception to ten points in Dolezalek's criticism of his paper (A., 1910, ii, 583), which he argues at length. J. F. S.

Regularities in the Steam Distillation of Organic Acids. ALBR. STEIN (*J. pr. Chem.*, 1913, [ii], 88, 83-89).—It has been shown by Naumann and Müller (A., 1901, i, 204) that at constant temperature and pressure the velocity of steam distillation of a volatile substance, as measured by the amount contained in unit volume of the distillate, is proportional to the amount of the substance in the distillation flask, provided that the volume of

liquid in the latter remains constant. From this the author deduces the equation $1/v \log a/(a-x) = c$, where a is the amount of the substance originally present in the distillation flask, v the volume of the distillate, x the amount of substance in the distillate, and c a constant, which is termed the distillation constant. The value of this constant has been determined for a number of organic acids, using a volume of 150 c.c.

In the case of acetic acid it is found that the velocity of distillation is independent of the concentration, and inversely proportional to the volume of the liquid in the distillation flask.

Substitution of a hydrogen atom in acetic acid by methyl increases the volatility, whilst substitution by phenyl, chlorine, carboxyl, and hydroxyl diminishes it in the order given.

Of the isomeric toluic acids, all of which have a greater volatility than phenylacetic acid, the ortho-compound is the most volatile and the para the least.

*iso*Butyric acid is more readily volatile than *n*-butyric acid.

F. B.

Small Rods for Preventing Superheating. E. P. HÄUSLER (*Zeitsch. angew. Chem.*, 1913, 26, 400).—The end of a glass rod is softened in the Bunsen flame and then a piece of platinum wire pushed into it. When the glass is cold the wire is bent backwards and forwards so as to break it off as near to the glass as possible. Such rods act extremely well in preventing the superheating of a boiling liquid.

T. S. P.

Polymorphism of Zinc. P. N. LASCHTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 552—557).—The author has measured the amounts of heat developed during the cooling of zinc in a tube of quartz glass from various temperatures ranging from 200° to 540° down to 15—15.5°. The curve having amounts of heat as ordinates and initial temperatures as abscissæ suddenly increases in steepness at 340—350°, which is in good agreement with the temperature of transformation as given by other observers. At the melting point, 419—420°, the curve rises vertically through a certain distance, and then becomes virtually a straight line. The heat of transformation is about 0.19 Cal. per gram-atom, and the latent heat of fusion about 1.73 Cal.

Although quartz exhibits a definite temperature of transformation at 575—580°, quartz glass contains no crystalline quartz, and hence shows no transformation point.

T. H. P.

Thermochemical Researches on Solution. III. NICOLAS DE KOLOSSOVSKI (*Bull. Acad. roy. Belg.*, 1913, 329—339. Compare this vol., ii, 22, 308).—The author has determined the heat of solution of sodium and potassium iodides and bromides in aqueous solutions of ethyl and methyl alcohols, the object of the work being to see if there existed in these cases the same regularity between the corresponding sodium and potassium salts as was found by Thomsen for aqueous solutions. For a 33.83% ethyl alcohol–water mixture,

that is, $200\text{H}_2\text{O} + 40\text{Et}\cdot\text{OH}$, the following heats of solution are found: $\text{NaBr} = -1866$ cal.; $\text{NaI} = +151$ cal.; $\text{KBr} = -6384$ cal., and $\text{KI} = -6076$ cal. The differences between the heats of solution of corresponding sodium and potassium salts are of the same order as the corresponding differences obtained for aqueous solutions; on the other hand, the differences between these figures are about double the values obtained for aqueous solutions. For a 30·77% methyl alcohol-water mixture, that is, $200\text{H}_2\text{O} + 50\text{Me}\cdot\text{OH}$, the following heats of solution were obtained: $\text{NaCl} = -2234$ cal.; $\text{NaNO}_3 = -6064$ cal.; $\text{KCl} = -5429$ cal., and $\text{KNO}_3 = -9300$ cal. The difference between the heats of solution of the corresponding sodium and potassium salts is -3850 cal., and between nitrate and chloride in each case -3215 cal.; this shows the additive nature of the heat of solution in alcohol-water solutions. The author then proceeds to examine certain solutions as to their suitability as freezing or cooling mixtures. It is shown that the following temperature lowerings are obtained: $50\text{NaCl} + 100\text{H}_2\text{O}$, $2\cdot5^\circ$; $50\text{NaCl} + 100\text{EtOH}$, $5\cdot5^\circ$; $100\text{C}_{12}\text{H}_{22}\text{O}_{11} + 100\text{H}_2\text{O}$, $2\cdot4^\circ$; $100\text{C}_{12}\text{H}_{22}\text{O}_{11} + 100\text{EtOH}$, $5\cdot5^\circ$; $100\text{NH}_4\text{NO}_3 + 100\text{H}_2\text{O}$, $25\cdot5^\circ$; $100\text{NH}_4\text{NO}_3 + 100\text{EtOH}$, $19\cdot0^\circ$; $50\text{KNO}_3 + 100\text{H}_2\text{O}$, $10\cdot9^\circ$; $50\text{KNO}_3 + 100\text{EtOH}$, $4\cdot1^\circ$; $100\text{EtOH} + 100\text{H}_2\text{O}$, $6\cdot4^\circ$; $100\text{PhOH} + 100$, 33·83% alcohol, $18\cdot4^\circ$; $100\text{PhOH} + 100$, 95% alcohol, $14\cdot4^\circ$; and $200\text{PhOH} + 100$, 95% alcohol, $22\cdot5^\circ$.

J. F. S.

Thermochemical Researches on Solution. IV. NICOLAS DE KOLOSSOVSKI (*Bull. Acad. Roy. Belg.*, 1913, 340—357. Compare last abstract).—The present paper deals with the relationship of the heat of solution in water and aqueous alcohol, and the degree of dissociation of the dissolved substance in these solvents; and for this purpose a number of heats of solution in water and 33·83% alcohol were determined. The following values were obtained: $\text{C}_3\text{H}_5(\text{OH})_3 + 200\text{H}_2\text{O} = +1339$ cal.; $\text{C}_3\text{H}_5(\text{OH})_3 + 200\text{H}_2\text{O} + 40\text{EtOH} = -412$ cal.; tannin + $400\text{H}_2\text{O} = +325$ cal.; tannin + $400\text{H}_2\text{O} + 80\text{EtOH} = +206$ cal.; $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{sucrose}) + 400\text{H}_2\text{O} = -913$ cal.; $\text{C}_{12}\text{H}_{22}\text{O}_{11} + 400\text{H}_2\text{O} + 80\text{EtOH} = -4290$ cal.; $\text{PhOH} + 200\text{H}_2\text{O} = -2730$ cal.; and $\text{PhOH} + 200\text{H}_2\text{O} + 40\text{EtOH} = -4578$ cal. On comparing these values with the corresponding values of strong electrolytes it is seen that there is no obvious difference in the heat change for electrolytes and non-electrolytes. The author shows that the heat of solution of phenol in alcohol-water mixture and in pure water furnishes evidence in favour of the existence of a phenol hydrate in the latter case, and not in the former. J. F. S.

Anhydrous Sodium Sulphate and Water. D. T. WILBER (*J. Physical Chem.*, 1913, 17, 556—557).—The dissolution of anhydrous sodium sulphate in water above the transition point ($32\cdot6^\circ$) is accompanied by a rise in temperature which is greater the higher the initial temperature. The explanation which connects the positive heat of solution with the falling solubility curve of the anhydrous salt is correct, but it does not explain the effect of the initial temperature on the temperature rise. Dammen suggested

an increasing heat of solution with rise in temperature, but it is sufficient explanation that the temperature rise depends on the ratio of the rate of dissolution to the rate at which heat is lost by radiation, etc., and that this ratio is higher at 90° than at 40°.

R. J. C.

Trouton's Quotient and the Heat of Vaporisation of Pure Substances Boiling at Low Temperatures. Data for Helium.

ROBERT DE FORCRAND (*Compt. rend.*, 1913, 156, 1809—1813).—The author has calculated the molecular heats of vaporisation of a number of substances of low b. p. (chlorine, radium emanation, oxygen, nitrogen, hydrogen, and helium) by means of his formula (this vol., ii, 556). The values obtained are in satisfactory agreement with those deduced from the vapour tension, and also with those obtained by direct experiment. Trouton's law only appears to be exact at moderate temperatures (from 300° to 900° absolute).

The method of calculating the molecular heat of vaporisation from measurement of vapour tension is fully explained in the instance of helium.

H. W.

A Safe Thermostat for Use with Coal-gas. WILLEM P. JONISSEN (*Chem. Weekblad*, 1913, 10, 532—537).—A description of a thermostat and stirrer actuated by hot air. The important features are use of "compo" pipe for the gas leads instead of indiarubber, and the complete enclosure of the gas-jets in a chamber of wire-gauze, on the principle of the Davy lamp.

A. J. W.

Constant Temperature Apparatus. FREDERICK H. DUPRÉ and PERCY V. DUPRÉ (*Analyst*, 1913, 38, 308—311).—An apparatus is described and figured, in which a constant temperature is obtained by regulating the pressure; this may be effected by cautiously withdrawing (or supplying) air after (or before) generating steam.

The apparatus consists of a boiler filled one-third with water, a reflux condenser, a water-jacketed pressure bulb, and a screw valve. When the latter is shut the apparatus is absolutely air-tight; a safety plug of fusible metal is supplied. The pressure determines the temperature of the steam evolved in the boiler, and so long as sufficient heat is supplied to keep the water boiling without producing more steam than can be dealt with by the condenser, the temperature remains practically constant.

L. DE K.

Molecular Constitution of the Free Surfaces of Liquids.

MADISON M. GARVER (*J. Physical Chem.*, 1913, 17, 386—389. Compare A., 1912, ii, 831).—The conclusion previously drawn from Maxwell's law of the distribution of molecular energies, namely, that attraction in the surface film of a liquid depends on the number of molecules irrespective of their mass, is now shown to be unnecessary. The equation is satisfied if it is assumed that the density of a liquid is determined solely by the molecular forces acting between individual molecules in the surface film. In the interior of the liquid the average force acting on a molecule in any

given direction is nil, but owing to the relatively crowded condition complexes are formed which act temporarily as single molecules.

The molecular weight in the surface film is the same as that of the saturated vapour.

R. J. C.

Gay and Ducelliez's Chemical Interpretation of Singular Points. NICOLAS DE KOLOSOSVSKI (*Bull. Soc. chim.*, 1913, [iv], 13, 648—650).—A criticism of Gay and Ducelliez's inferences (compare this vol., ii, 387).

W. G.

Significance of the Relationship between Molecular Cohesion and the Product of the Molecular Weight and the Number of Valencies. ALBERT P. MATHEWS (*J. Physical Chem.*, 1913, 17, 481—500. Compare this vol., ii, 300, 494, 495).—According to Drude, the electron couples constituting molecules are of two kinds, namely, those of the atoms which when added together give the molecular weight, and the valency electrons, which have a different degree of liberty and can vibrate synchronously with light. Pascal has shown (A., 1911, ii, 367, 679) that magnetic susceptibility is a function of atomic weight and valency; thus refractive index, diamagnetism, and molecular cohesion are cognate properties.

The fact that cohesion is determined by the number of electron couples (atomic and valency) in the molecule suggests that it is electrostatic or electromagnetic in nature. The author adopts the latter view, and supposes that magnetic attraction is molecular cohesion made apparent at distances more than molecular by reason of the orientation of polarised molecules.

If a molecule is of such a nature that its electron couples co-operate to produce polarity, it is paramagnetic, but if the molecule has many poles it is diamagnetic, and its magnetic field coincides with its cohesive field.

In non-magnetic substances the cohesive field is completely neutralised by the surrounding molecules.

R. J. C.

Do Molecules Attract Cohesively Inversely as the Square of the Distance? ALBERT P. MATHEWS (*J. Physical Chem.*, 1913, 17, 520—535. Compare preceding abstract).—The empirical equation, $A = L - E = k(\frac{3}{d} - \frac{3}{D})$, where A represents the internal latent heat employed in overcoming molecular cohesion on passing from liquid at density D to vapour at density d , was considered by Mills (A., 1911, ii, 711; 1912, ii, 1041) as evidence that molecular cohesion, like gravitation, follows an inverse square law. Mills' equation is not valid in the neighbourhood of the critical temperature, whereas the equation given by van der Waals is valid only at the critical temperature. This equation, $L - E = a(d - D)$, indicates, according to Sutherland, that molecular cohesion varies inversely as the fourth power of the distance between molecular centres.

The total latent heat L must be equal to the sum of three factors, namely, E , the external work, A , the work against molecular cohesion, and I , the energy absorbed in expanding the actual

molecules and increasing their rotation; thus the correct equation should be $L - E - I = a(d - D)$ on Sutherland's hypothesis, and in any case Mills' equation cannot be correct, as it takes no account of I , so that the inference drawn from it, that the molecules attract inversely as the square of the distance, is not justified. The equation $L - E - I = a(d - D)$ reduces to that of van der Waals near the critical temperature, where I is very small. It cannot be verified at other temperatures in the absence of an independent estimate of the value of I , but in accordance with it the ratio $(L - E)/(d - D)$ increases progressively from a on passing from the critical to lower temperatures. The value of I for hexane is nil at the critical point (234.5°) and 28.21 Cal. at 0° .

It is urged that the known variations in the constant b of van der Waals' equation indicate that the factor I cannot be neglected. At low temperatures, when b decreases on vaporisation it must be supposed that association or quasi-association occurs in the vapour and I retains a positive value.

R. J. C.

Fluidity and the Hydrate Theory. II. EUGENE C. BINGHAM, GEORGE F. WHITE, ADRIAN THOMAS, and J. L. CADWELL (*Zeitsch. physikal. Chem.*, 1913, 83, 641—673. Compare A., 1912, ii, 1144).—A continuation of the previous work; the authors have measured the fluidity of the following series of binary liquid mixtures at a series of temperatures: Ethyl alcohol and water, acetic acid and water, methyl alcohol and water, formic acid and water, *n*-hexane and diisomyl, methyl alcohol and ethyl alcohol, acetic acid and ethyl alcohol, and also the ternary mixtures ethyl alcohol, water, and acetic acid, and ethyl alcohol, methyl alcohol, and water. The measurements of other observers are recorded, compared with the authors' values, and criticised. An hypothesis is put forward to explain the relationship between fluidity and other physico-chemical properties. It is shown that in comparing the fluidity of mixtures, volume concentration must be used instead of the usually adopted weight concentration. It is also shown that normally the fluidity concentration curve is linear, and that changes from the linear curve in certain mixtures can be explained by chemical changes, association, etc. The cases examined indicate that many so-called solvates are, strictly speaking, chemical compounds of one molecule of each of the components of the mixture, and in this they are directly opposed to the general theory that a solvate is undetermined in its composition. This is explained by the statement that at any given moment only a small fraction of the components are combined, and that an equilibrium exists between the compound and the components. It is shown that taking μ_∞ as a measure of the anions and cations in the ionic migration, in ethyl alcohol-water mixtures this value decreases when the concentration of the alcohol is slowly increased, but no minimum is to be found which corresponds with the fluidity minimum. Assuming that the "atmosphere" surrounding the ions is of uniform size it would follow that the conductivity would be proportional to the fluidity. But in mixtures with small fluidity the components are combined to the

largest extent; consequently, the atmosphere surrounding these atoms or groups is diminished, and the ionic velocity is correspondingly large. It is also shown that when an acid and an alcohol are mixed an additive compound of the two components is first formed, and that this then decomposes to form the ester. Also it is shown that a maximum in a viscosity-weight concentration curve does not necessarily give the composition of the solvate; consequently, until some other evidence is forthcoming as to the existence of hydrates in solution than this, the results must be received cautiously.

J. F. S.

Association in Some Gaseous Mixtures. ALFRED SCHULZE (*Ber. Deut. physikal. Ges.*, 1913, 15, 488—496. Compare A., 1912, ii, 108).—Experiments are described on the vapour pressure of the following vapour mixtures: acetone-chloroform, ethyl ether-benzene, benzene-chloroform, and ethyl ether-carbon disulphide. It is shown that on mixing acetone and chloroform a mutual association takes place, and at 80° under a total pressure of 1 atm. the two substances combine to the extent of 0.37 mol. %. From this it follows of necessity that the same compound exists in the liquid mixture and to a much larger extent, as has been shown by the divergence of the mixture from the mixture laws. With regard to the mixtures ethyl ether-benzene and benzene-chloroform a chemical compound of the two substances could also be detected in the gaseous phase. By the same method it is shown that in the mixture ethyl ether-carbon disulphide on account of the increase in pressure on mixing the vapours that carbon disulphide must be strongly associated; probably ter- or quadri-molecular complexes are present. Finally, a series of other properties are detailed, which allow of conclusions being drawn as to association in liquids and vapours.

J. F. S.

Related Absorption Curves. I. WERNER MECKLENBURG (*Zeitsch. physikal. Chem.*, 1913, 83, 609—624. Compare A., 1912, ii, 355).—The author had previously shown that if the absorption curves of phosphoric acid by stannic oxide are plotted for different temperatures, a series of curves are obtained such that if one be taken as the normal curve then by multiplying the ordinate values of that curve by a given figure and leaving the abscissæ values alone the other curves can be obtained. Such a series of curves the author calls "related" (affine) curves. The object of the present paper is to see if such curves are general for other absorbing colloids, and for this purpose the absorption curves of arsenious oxide by ferric hydroxide gels at a number of temperatures is determined. It is shown here that such related curves are obtained. The meaning of the relationship between the curves is held to be due to the specific surface of the adsorbent, and consequently the constants for the various curves can be taken as a relative measure of the specific surface of the different specimens of the adsorbent. It is also shown that similar related curves can be obtained when a given substance is adsorbed by a series of different adsorbing colloids.

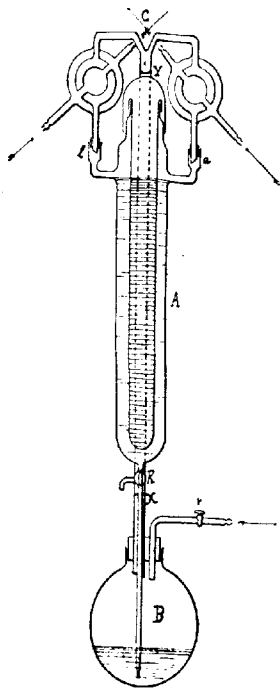
J. F. S.

Adsorption. IV. GERHARD C. SCHMIDT (*Zeitsch. physikal. Chem.*, 1913, **83**, 674—682. Compare A., 1910, ii, 1041; 1911, ii, 969; 1912, ii, 233).—The author gives a new and stricter proof of his adsorption isothermal formula $(a-x)/v \cdot S = Kc^A \cdot (S-x)^x$, in which x represents the quantity of adsorbed substance, v the volume, $(a-x)/v$ the concentration, S the concentration at saturation, and A and K constants. The analogy between adsorption and reactions of the first and second orders is illustrated by consideration of the decomposition of calcium carbonate in the absence and presence of carbon dioxide. It is shown that absorption of gases runs parallel to the power of those gases in reducing and destroying the fluorescence of iodine and mercury vapours. J. F. S.

Tension of Metal Ammonias. FRITZ EPHRAIM (*Zeitsch. physikal. Chem.*, 1913, **84**, 98—100).—Polemical: an answer to Biltz (this vol., ii, 129, 130). J. F. S.

An Analytical Dialyser. LADISLAS KOPACZEWSKI (*Compt. rend.*, 1913, **156**, 1853—1855).—The author has devised an apparatus in which (1) rapid dialysis in a stream of pure water, (2) distillation of the water, and (3) condensation of the dialysable portion can be effected. It may be readily understood from the annexed diagram.

A is a modified dialyser provided with a glass tube; by means of the three-way cock, R , communication can be established between A and the flask B , or water may be drawn off by the lateral tube to enable the operator to determine the end of the reaction. The Jena-glass flask, B , is provided with a cork carrying three tubes; two of these, made of glass, communicate with the dialyser and pump respectively, whilst the third, of tin, leads to the condensers. The latter are connected by a Y-tube, and so arranged that the water condensed in them flows into A . In use, the flask is filled with a suitable quantity of water, and the dialyser placed in position. The apparatus is then exhausted through the stopcock r , and the latter closed. The flask is heated at about 40° . Under these circumstances between three and four litres of water distil per day, and the water in the dialyser is renewed from ten to twenty times.



It is claimed that dialyses can be effected much more rapidly in this apparatus than in the usual manner, and further, that, if the dialyser is removed, the apparatus can be used for the preparation of water in a high state of purity.

H. W.

Passage of Nascent Hydrogen through Iron M. BELLATI and SILVIO LUSSANA (*Nuovo Cim.*, 1913, [vi], 5, i, 389—392).—The recent paper of Charpy and Bonnerot (*A.*, 1912, ii, 336) only confirms the authors' results published twenty years since (*Atti Istituto Veneto*, 1888—1891).

R. V. S.

Osmotic Pressure of Colloids. IV. The Theory of Colloidal Electrolytes. WILHELM BILTZ (*Zeitsch. physikal. Chem.*, 1913, 83, 625—639. Compare *A.*, 1910, ii, 22, 693; 1911, ii, 702).—The author criticises and compares the views of Donnan and Harris (*T.*, 1911, 99, 1554) and Donnan (*A.*, 1911, ii, 848) with his own. It is shown that in connexion with the wandering in of electrolytes in the measurement of osmotic pressure of colour substances against water of equal electro-conductivity, that the theories of Donnan and the author agree qualitatively, and in some cases quantitatively. Hydrolysis is discussed in connexion with the older theories and with Donnan's theory of membrane hydrolysis chiefly in the following points: (a) hydrolysis in the preparation and purification of colloids; (b) lowering of osmotic pressure by hydrolysis, and the accompanying formation and polymerisation of free colour acids; (c) driving back of hydrolysis in osmotic experiments by the addition of the products of hydrolysis. The author concludes that even in the light of the more general theory of Donnan, his conclusions, as stated in his last paper (*loc. cit.*) with regard to characteristics of the solutions of colour substances, sufficiently express the observed conditions.

J. F. S.

Dispersological Theory of True Solutions. PETR P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloid*, 1913, 12, 298—308. Compare this vol., ii, 307).—The author starts from the statement that solids are practically insoluble in those liquids in which they are unable to form solvates, and toward which they are chemically indifferent. The conclusion is drawn that solution in water is brought about by a weakened (dynamic chemical) linking between the water and the dissolved substance; the intensity of the linking must lie between fixed limits, an increase leading to static chemical linking (that is, the formation of definite hydrates) as well as a diminution causing a diminished solubility. From a consideration of the ultramicroscopic structure of solutions the author comes to the conclusion that the dimensions of the viscosity of the solvate particle tend to approach those of the particles of the solvate without ever actually reaching them. In the ideal case at the maximum of the solubility curve the dissolved particles have their maximum dimensions and minimum density, and at this point the viscosity of the dissolved particles most nearly approaches the viscosity of the solvent particles. In connexion with the mechanism of solutions it is shown

that the process of solution consists in a diminution of the surface energy by means of a diminution of the surface tension and a compensating of the tendency to contract by the residual surface energy, by means of the kinetic energy of the solution. In a typical case of a true solution the contractive tendency of the surface energy is entirely compensated by the kinetic energy of the solvent, and consequently the homogeneous distribution of the dissolved substance cannot change with time. Similarly, in the case of a substance which is absolutely indifferent to the solvent the contractive tendency of the extremely large surface energy cannot be compensated by the kinetic energy of the solvent, and consequently such solutions can only maintain their homogeneous distribution for any length of time when they are very dilute. J. F. S.

Electrolytic Dissociation of a Salt Governed by the Mass Law. PAUL TH. MÜLLER and R. ROMANN (*Compt. rend.*, 1913, 156, 1889—1891).—It has been assumed recently that the failure of salts and good electrolytes in general to dissociate electrolytically in accordance with the mass law, is due to gradual hydration of the ions which accompanies dilution. If this is so the mobility of the ions will become constant when hydration is complete, and the conductivity will then no longer depend only on the ionisation, and under these conditions the mass law should govern the change. This hypothesis has been verified for piperidine cyanoacetate. T. A. H.

A New Theory of Allotropy. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1913, 83, 728—734).—Polemical against Smits (compare Smits, A., 1910, ii, 195, 400; this vol., ii, 393; Tammann, A., 1913, ii, 193). J. F. S.

Colloidal Suspension of Graphite. HENRY L. DOYLE (*J. Physical Chem.*, 1913, 17, 390—401).—Crystalloids, such as sodium chloride, sodium hydroxide, acetic acid, etc., have no appreciable influence on the rate of settling of suspensions of bone-black and graphite. Bone black and graphite decolorise saturated solutions of iodine in water, but iodine has no influence on the rate of settling of these substances in benzene and absolute alcohol.

Good suspensions of graphite and bone-black in water were obtained by the use of caseinogen dissolved in sodium phosphate, dilute ferric acetate which had been boiled to promote hydrolysis, and sodium oleate. Concentrated sugar solutions, gelatin solutions, and an ammoniacal suspension of catechu have a little influence in stabilising suspensions of graphite, which in the case of catechu is increased by the presence of iron oxide.

An excellent suspension of graphite in oil was obtained by the use of a dry iron soap prepared by heating ferric chloride solution with sodium oleate. Sodium and magnesium oleates and precipitated ferric hydroxide give good suspensions, but only in presence of a small proportion of water. A dark gummy product obtained by heating "paraffin" in air had some effect, but resin and shellac were without influence.

A sample of Acheson's "Aquadag" was found to contain 3.2% of ferric oxide and 1.2% of copper in a total ash of 8%.

R. J. C.

Indirect Analysis of a Ferric Oxide Gel. HARRY B. WEISER (*J. Physical Chem.*, 1913, 17, 536—555).—The calculation of the composition of a deposited gel from that of its mother liquor (Bancroft, A., 1905, ii, 685) depends on the assumption that one constituent of the mother liquor is entirely absent from the gel. Gelatinous ferric hydroxide precipitated from a known amount of ferric chloride solution by a known excess of sodium hydroxide solution cannot be analysed by this method, as both sodium and chlorine are found in the gel. A modification of the method is possible in this case, as the hydroxide is matted into a compact mass by long-continued centrifuging, and the mother liquor may be decanted practically without loss. The weight and composition of the mother liquor are the data necessary for calculating the composition of the gel. The indirect method avoids the estimation of small amounts of sodium and chlorine in presence of excess of iron.

The quantities of sodium hydroxide, chloride, and water adsorbed in ferric hydroxide gel vary widely with the composition of the mother liquor and the age and amount of centrifugal treatment of the gel. The absorption of chloride is diminished by an excess of sodium hydroxide.

R. J. C.

Proof of the Applicability of the Boyle-Mariotte and Gay-Lussac Laws to Emulsions. B. ILJIN (*Zetsch. physikal. Chem.*, 1913, 83, 592—598).—The author has examined emulsions of gamboge in water, castor oil, and gum arabic in water, and from the results draws the conclusions that in emulsions the variation in concentration follows the theoretical laws within the limits of experimental error; also that at the concentrations employed in the work the compressibility ratio β/β_0 is very nearly unity, or, in other words, that the movements of a given particle are quite independent of the movements of the other particles.

J. F. S.

Theory of Emulsification. V. WILDER D. BANCROFT (*J. Physical Chem.*, 1913, 17, 501—519. Compare this vol., ii, 121).—In an emulsion the surface film surrounding the dispersed drops must be considered as a separate phase. This film adsorbs each of the two liquid phases, and its surface tension is not the same on each side. The film becomes concave, and envelopes the liquid on the side with the higher surface tension. Hence a hydrophile colloid will make water the dispersing phase, and a hydrophobe colloid will make water the dispersed phase.

Examples of emulsions in which water is dispersed are lanolin (which contains 25% of water), emulsions of water in mineral oil containing resin, greases, or solidified oils in which a lime soap is usually the emulsifying agent, and ready-mixed paints to which water has been added to keep the solid ingredients in suspension.

In the last case the dispersing phase is linseed oil, and the emulsifying agent probably rosin. Experiments made by F. R. Newman showed that an emulsion of water in white lead paint could contain as much as 70% of water. Water can be dispersed in carbon disulphide to the extent of 90%, using magnesium oleate with a little sodium oleate as protective colloid. In order to emulsify two liquids which are completely miscible it is necessary to add some soluble substance which will cause the two liquids to separate, as well as an emulsifying colloid or powder. The cracking of emulsions with age is often due to the shrinkage of the jelly-like colloidal film. In some emulsions, however, the protective film is a layer of ions due to an electrical charge.

R. J. C.

Kinetics of Chemical Reactions of the First, Second, and Third Orders. V. Egor I. Orlov (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 457—488. Compare this vol., ii, 127, 128).—The author arrives analytically at the following results.

The chemical reactions characterised by the fundamental differential equations (I) $dx/dt = k(A - x)$, (II) $dx/dt = k(A - x)(B + x)$, and (III) $dx/dt = k(A - x)(B - x)$ or $dx/dt = k(A - x)$, represent the summation of at least three reactions, the observed values of x being composite magnitudes.

Mathematical analysis of the equations (II) and (III) renders possible their resolution into: (1) An equation of a reaction of the first order, $dx_1/dt = k_1(A - x_1)$. (2) An equation representing the action of a newly-formed substance, different from A , and increasing in concentration x^1 ; on its formation, the new compound immediately decomposes into fresh groupings. The reaction proceeds with velocity k_2 , and is represented in the fully developed differential equation by the term $+k_2x^1(A - x_1)$. (3) An equation of the counter-reaction of the new compound x^1 , this proceeding with velocity k_3 , and being represented in the complete equation by the term $-k_3x^1(A - x_1)$.

For a reaction with the fundamental differential equation, $dx/dt = k(A - x)(B + x)$, k_2 is always greater than k_3 and $k_2 - k_3 = k$. For one with the equation $dx/dt = k(A - x)^2$ or

$$dx/dt = k(A - x)(B - x),$$

k_2 is always less than k_3 and $k_2 - k_3 = -k$, whilst for one with the equation $dx/dt = k(A - x)$, k_2 is equal to k_3 .

The term $k_1(A - x_1)$ of the complete equation is present in every differential equation representing a chemical reaction, and characterises a process of change of the initial substance into one of different nature; for instance, an ionised into a non-ionised complex. This change is a time-change, and when complete is immediately followed by further resolution into new groups or ionic groupings. The interaction of these new groups with the remaining initial compound and the corresponding counter-reaction proceed simultaneously with the first reaction, and are also time-reactions.

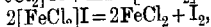
The velocity constant k of the fundamental equation represents the difference $k_2 - k_3$, and may be either positive, or negative, or zero.

T. H. P

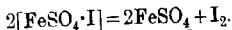
Kinetics of Reactions of the Second and Third Orders. VI. EGOR I. ORLOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 489—511. Compare this vol., ii, 127, 128).—The author considers the derivation of the differential equation $dx/dt = k(A - mx)^3$ from $dx/dt = k(A - x)^3 + k_1\phi(x)$. Writing k_1 for $k(1 - m)$, k_2 for $1 + m$, and k_3 for $1 + m + m^2$, it is shown that $\phi(x) = x\{3A(A - k_2x) + k_3x^2\}$. So that, $dx/dt = k(A - mx)^3$ is derived from $dx/dt = k(A - x)^3 + k_1x\{3A(A - k_2x) + k_3x^2\}$. The second term of the right-hand side has a positive sign if m is less than 1, whereas if m is greater than 1 the equation becomes

$$dx/dt = k(A - x)^3 - k_1x\{3A(A - k_2x) + k_3x^2\}.$$

The reactions (1) $2\text{FeCl}_3 + 2\text{KI} = 2\text{FeCl}_2 + 2\text{KCl} + \text{I}_2$ and (2) $\text{Fe}_2(\text{SO}_4)_3 + 2\text{KI} = 2\text{FeSO}_4 + \text{K}_2\text{SO}_4 + \text{I}_2$ (compare Seubert and Dorrer, A., 1894, ii, 140, 191) are shown to be capable of representation thus: (1) $[\text{FeCl}_2]\text{Cl} + \text{KI} = [\text{FeCl}_2]\text{I} + \text{KCl}$ and



and (2) $\left[\begin{smallmatrix} \text{FeSO}_4 \\ \text{FeSO}_4 \end{smallmatrix} \right] \text{SO}_4 + 2\text{KI} = 2[\text{FeSO}_4\cdot\text{I}] + \text{K}_2\text{SO}_4$ and



Since, on the one hand, the reaction does not proceed to completion but attains a limit, and, on the other, the iodine separated combines, as it is liberated, with potassium iodide to form the complex KI_3 , and so removes a corresponding quantity of potassium iodide from the sphere of the reaction, it is regarded as justifiable to apply to the process either the equation

$$dx/dt = k(A - mx)(B - mx)$$

or $dx/dt = k(A - mx)^2$. The integral of this equation under such conditions that $x=0$ when $t=0$ is $mk = mx/tA(A - mx)$, where k and m are constants and A the amount of iodine corresponding with the whole of the ferric chloride or sulphate, independently of whether the whole or only part of the salt takes part in the reaction. The magnitude of m depends on the concentration of the potassium iodide, and is, in most cases, greater than 1, so that in the differential equation $dx/dt = k(A - x)^3 + k_1\phi(x)$ the constant k_1 is negative in sign. Hence the change proceeds with retardation of the principal reaction, $k(A - x)^3$, owing to union of the iodine and potassium iodide to form the complex KI_3 and to its reversibility. The magnitude of k increases in approximate proportion to the square of the concentration of the potassium iodide. When k_1 is negative the smaller the concentration of potassium iodide the greater is the absolute magnitude of k_1 and the more marked will be the negative catalysis.

Bodenstein and Kranendieck (A., 1912, ii, 747) attempted to explain the results of their investigations on the decomposition of sulphur trioxide in quartz vessels at high temperatures by assuming that the course of the reaction is represented by an equation of the first order, $dx/dt = k(A - x) - k_1x$. Such an assumption is open to criticism, especially as it is not easy to explain why, under certain conditions, a reaction of the third order should proceed as one of the first order. To explain the divergence of this reaction from the usual type, the author applies the equation for a

reaction of the third order in its general form, namely,

$$dx/dt = k(A - mx)^3,$$

integration of which gives $2A^2mk = mx(2A - mx)/(A - mx)^3$. Re-calculation of Bodenstein and Kranendieck's experimental results gives constant values for A^2mk .

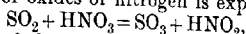
In his investigations on the oxidation of sulphur dioxide in aqueous and dilute sulphuric acid solutions by means of oxides of nitrogen, Trautz (A., 1904, ii, 328) obtained time-curves which he could not explain satisfactorily. The author shows that application of the differential equation in its general form,

$$dx/dt = k(A - mx)^2,$$

and calculation of the corresponding integral,

$$Amk = mx/t(A - mx),$$

give constant results. The oxidation of sulphur dioxide in presence of oxides of nitrogen is, indeed, a reaction of the second order, complicated by negative catalysis. The influence of the latter is explained by the author as follows: The oxidation of sulphur dioxide in presence of oxides of nitrogen is expressed by



which is a reaction of the second order. Hence the reaction would proceed according to the equation $dx/dt = k(A - x)^2$ if the nitrous acid did not remain in the solution and if other reactions did not proceed at the same time. But the nitrous acid undergoes the change represented by: $3\text{HNO}_2 \rightleftharpoons 2\text{NO} + \text{HNO}_3 + \text{H}_2\text{O}$, the nitric acid then oxidising SO_2 and being itself reduced to nitrous acid, whilst 2NO is oxidised in the atmosphere to 2NO_2 , which then dissolves again, giving $\text{HNO}_3 + \text{HNO}_2$. The equilibrium between nitrous acid, nitric oxide, nitric acid, and water is established, not instantaneously, but only after a certain time, and it is to this circumstance that the negative catalysis of the reaction is due.

T. H. P.

Kinetics of Chemical Reactions of Oxidation, Combination, and Deoxidation. VII. EGOR I. ORLOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 511—551).—The author applies the results previously obtained to elucidate the mechanism of various oxidation changes (compare this vol., ii, 127, 128).

The oxidation of hydriodic acid by potassium dichromate in presence of sulphuric acid is a reaction of the first order proceeding according to the equation $dx/dt = k(A - mx)$, the value of m being 1.01—1.05. If the concentrations of the potassium iodide and sulphuric acid are each doubled, the value of k is increased approximately $8^{(23)}$ times; further, if the concentration of the potassium iodide only is halved, k is almost doubled, whereas the reaction velocity is increased sixteen times (2^4) when the concentration of the sulphuric acid is doubled.

In presence of arsenic acid the oxidation of hydriodic acid by potassium dichromate is a unimolecular reaction of either the first or the second order, being represented by $dx/dt = k(A - mx)$ or $dx/dt = k(A - mx)(B + mx)$. When the second law holds, it is

assumed that an intermediate compound is formed by the chromate and the iodine liberated, this being, on the one hand, a double compound of iodine with a salt of trivalent chromium, and on the other a compound having the properties of hexavalent chromium and hence possessing oxidising properties.

In the oxidation of potassium iodide by potassium bromate in presence of arsenic acid, no direct proportionality exists between the magnitudes of the velocity constant and the concentrations of the iodide and the arsenic acid, the action of the bromic acid being, not quantitative, but only partial. The oxidation by bromic acid in presence of potassium dichromate, ferric chloride, or sodium tungstate, and oxidation by hydrogen peroxide in presence of acetic acid either alone or together with potassium dichromate, ferric chloride, sodium tungstate, or ammonium molybdate have also been studied.

The oxidation of hydriodic acid by means of bromic acid, hydrogen peroxide, or potassium dichromate in an acid medium and either with or without an accelerator may be regarded as a chemical process obeying a law expressed by the general equation $dx/dt = k(A - mx)$, which has been shown previously to be derived from $dx/dt = k(A - x) \pm k_1x$. This equation shows that the process comprises, besides the principal reaction of the first order expressed by $k(A - x)$, also another reaction with velocity k_1 , which may either accelerate the principal reaction, k_1 being then positive, or retard it, in which case k_1 is negative; in the general equation this difference is shown by the factor m being less or greater than 1. In presence of an accelerator the values of both k and k_1 are altered.

T. H. P.

The Effect of Incombustible Dusts on the Explosion of Gases. HAROLD B. DIXON and COLIN CAMPBELL (*J. Soc. Chem. Ind.*, 1913, **32**, 684—687).—The experimental results which led Abel to his view that the presence of inert dust could promote the combustion of firedamp by a catalytic surface effect and so increase the danger of explosion, are shown to have been due to incomplete mixing of the firedamp and air used; there could thus be streams of gas richer in combustible constituents than the samples drawn for analysis. In experiments by the authors it was found impossible to render explosive, by the addition of incombustible dust, a gaseous mixture which under ordinary conditions would not propagate flame when sparked. Even heating such a mixture by an electrically-heated platinum wire did not render it explosive.

The experiment of Mallard and Le Chatelier (*Ann. des. Mines*, 1882) may easily be modified to show the inertness of magnesia and other incombustible dusts. A glass tube 5 feet long and 3 inches in diameter is fed from below with a mixture of gas and air from a Mecker burner and an adjustable orifice, whilst a Bunsen flame burns across the upper end. When the gaseous mixture is just below the explosive limit particles of magnesia (heated by passage through the Bunsen flame) carry down a small flame cap with them, but when the mixture is above this limit and would propa-

gate a flame if it was not moving upwards faster than the flame can travel down, a heated particle carries a real flame in its wake as it falls, and the flame spreads outwards in an inverted cone. When the mixture is just strong enough to propagate, a flame downwards the heterogeneity of the mixture is revealed by curious round films of flame which slide over one another. D. F. T.

Reactions in Aqueous and Colloidal Systems. WILLIAM P. DREAPER (*J. Soc. Chem. Ind.*, 1913, 32, 678-684).—Experiments on the formation of insoluble substances, in which the reacting solutions are contained in glass capillary tubes, demonstrate the fact that stratification can occur in the absence of any gel. Stratified layers were obtained of lead chloride, lead ferrocyanide, lead sulphate, silver ferrocyanide, barium sulphate, and barium carbonate. In one experiment a crystal of lead chloride 4 mm. in length was produced as one layer. Precipitation in the form of spherulites was not observed. The results indicate that the presence of a gel is not necessary to stratification, but that the diffusion process is primarily responsible; local supersaturation may exert some effect, but this can only be subsidiary because if a tube of stratified lead chloride crystals is heated until the precipitate dissolves, recrystallisation without stratification occurs on cooling.

When potassium sulphate is allowed to diffuse into a capillary tube containing barium chloride solution in which gelatin has been dissolved (or ammonium chloride may replace the gelatin) an opaque band of deposited barium sulphate appears to advance through the tube, leaving a clear space behind. This appearance is due to the gradual change of the finely divided opaque precipitate into an almost invisible crystalline salt, which could be easily examined under the microscope. D. F. T.

Colorimetric Investigation of Neutral Salt Action. II. Hydrogen Bromide. BOHDAN VON SZYSZKOWSKI (*Zeitsch. physikal. Chem.*, 1913, 84, 91-97. Compare A., 1912, ii, 146).—The author has investigated the influence of sodium and potassium bromides on the colour reaction between methyl-orange and hydrogen bromide. The influence of these substances is compared with the corresponding influence of chlorides on hydrogen chloride, and it is shown that the sodium ion has a stronger influence than the potassium ion, and bromine than chlorine, the general nature of the influence being additive. But with sodium bromide the additive character vanishes entirely, and a very much smaller effect is observed; this is explained by assuming a removal of hydrogen bromide by the formation of a complex of the type $n\text{NaBr} \cdot \text{HBr}$. J. F. S.

Equilibria in Systems Containing Alcohols, Salts, and Water, Including a New Method of Alcohol Analysis. GEORGE B. FRANKFORTER and FRANCIS C. FEARY (*J. Physical Chem.*, 1913, 17, 402-473).—The equilibrium diagrams of the ternary systems of water with methyl alcohol-potassium carbonate, ethyl alcohol-potassium carbonate and fluoride, propyl alcohol-potassium carbon-

ate and fluoride and sodium chloride have been plotted in triangular co-ordinates. Each of these six systems becomes heterogeneous within certain limits of concentration, and the alcohol phase may be rendered visible with phenolphthalein in the case of potassium carbonate systems and with "spirit-blue" in the others. The tie lines are straight, whether in triangular or rectangular co-ordinates.

In general, the solubility of the hydrated salts in absolute alcohol is about the same as in 60–70% alcohol, and greater than in alcohol of intermediate dilutions. The influence of temperature on the position of the binodal curves is small with methyl and ethyl alcohols, but considerable in propyl alcohol mixtures, particularly with sodium chloride. Propyl alcohol has a minimum solubility in 2.28% sodium chloride solution at about 37°. Some of the heterogeneous solutions had both upper and lower critical temperatures, outside of which they were homogeneous.

The relative salting out powers of potassium fluoride and carbonate for ethyl and propyl alcohols are opposite, and sodium chloride, which is a good precipitant for propyl alcohol, does not affect ethyl alcohol. The precipitating action does not depend on the ions of the salt, but rather on its affinity for water.

Anhydrous potassium fluoride is an excellent dehydrant for alcohols, acting rapidly on account of its solubility in the alcohols, and absorbing a large proportion of water (62%) to form its lowest hydrate, $\text{KF} \cdot 2\text{H}_2\text{O}$. The limit of dehydration of ethyl alcohol is at 97.5% when the vapour pressure, 3.5 mm., corresponds with that of the hydrate, $\text{KF} \cdot 2\text{H}_2\text{O}$.

Saturated potassium fluoride solution is superior to saturated potassium carbonate as a dehydrant as it has a lower vapour pressure.

Ethyl alcohol in aqueous solution may be estimated by adding sufficient potassium fluoride to salt out part of the alcohol, and then adding water, drop by drop, until the solution is just homogeneous again at 25°. The proportion of alcohol is found by reference to the solubility curve of the salt in alcohol-water mixtures.

The method is not applicable to liquors such as beer, which contain dissolved solids, but is fairly accurate in presence of small proportions of methyl alcohol.

R. J. C.

The Velocity of Evolution of Oxygen from Bleaching Powder Solutions in Presence of Small Quantities of Cobalt Nitrate and the Influence of Different Compounds on it. N. M. BELL (*Zeitsch. anorg. Chem.*, 1913, 82, 145–163).—An apparatus is described by means of which a 0.5078*N*-solution of cobalt nitrate may be added to a solution of bleaching powder in a thermostat, and the volume of escaping oxygen measured. The velocity accords well with a unimolecular reaction, but is modified by shaking and by the order in which the solutions are mixed. Acids accelerate the reaction by about one-half for *N*/50-solutions of the acid, and alkalis retard it by one-half for a *N*/2000-solution. Salts accelerate or retard it, and a relation between the nature of the salt and its catalytic influence has not been found. Nickel sulphate has about

the same influence as cobalt nitrate, but ferrous sulphate has only about 1.5% of the catalytic influence of the cobalt salt. C. H. D.

Piezoechemical Studies. X. The Influence of Pressure on the Velocity of Reaction of Condensed Systems. I. ERNST COHEN and R. B. DE BOER (*Zeitsch. physikal. Chem.*, 1913, **84**, 41—82. Compare last abstract).—The authors give a long critical review of the older work on the influence of pressure on the velocity of chemical reactions, and follow this with a description of experiments on the velocity of hydrolysis of sucrose at 25° by *N*/8- and *N*/16-hydrochloric acid at pressures varying from 1 to 1500 atms. The authors have also determined the compressibility of sucrose solutions, and this value is used in the calculations of the velocity constant. The measurements by this method can be made with the same accuracy as at ordinary pressures. It is shown that the reaction velocity is decreased by 8% at a pressure of 500 atms., by 19% at 1000 atms., and 26% at 1500 atms. The influence of pressure can be expressed by the equation $d\log k/dp = \text{const.}$ and also by the linear equation $k_p = a + bp$. The compressibility of a solution of sucrose containing 20 grams in 100 c.c. of solution at 25° is found to be 238.5—423.1 atms. $\beta \times 10^6 = 36.7$, 1252.0—1509.0 atms. $\beta \times 10^6 = 29.1$. J. F. S.

Hydrolysis of Esters of Substituted Aliphatic Acids. VI. Saponification by Sodium Hydroxide of Hydroxy- and Alkyl-oxyacetates and -propionates. E. W. DEAN (*Amer. J. Sci.*, 1913, [iv], **35**, 605—610. Compare Findlay and others, T., 1905, **87**, 747; 1909, **95**, 1004).—The velocity of saponification by sodium hydroxide at 0° and 25° of the following ethyl esters has been determined: Ethyl acetate, glycolate, methoxyacetate, ethoxyacetate, propoxyacetate, propionate, lactate, glycerate, α -ethoxypropionate, and β -ethoxypropionate.

The presence of an hydroxyl group in aliphatic esters produces an acceleration in the velocity of saponification, which, however, is variable in its magnitude. The presence of alkyloxy-groups has a very varying effect, in some cases resulting in a considerable acceleration, in others in a slight retardation. With alkyloxy-esters of similar constitution the velocity of saponification decreases as the molecular weight of the alkyloxy-group increases.

β -Substituted esters are saponified less rapidly than the α -isomerides, in this respect behaving the same as in acid hydrolysis; generally, however, the relative velocities of saponification of the esters studied are quite different from the relative velocities of their acid hydrolysis.

The velocity of saponification seems to be closely connected with the strength of the acid from which the ester is derived; a quantitative relation could not be found at present, but, in general, the stronger the acid the greater the velocity of saponification.

T. S. P.

The Forces which Determine the Velocity of Removal of Soluble Colloids from Colloidal Media in Aqueous Solutions. T. BRAILSFORD ROBERTSON (*Pflüger's Archiv*, 1913, 152, 524—531. Compare A., 1910, i, 528).—The author shows that the velocity of extraction of proteins from colloidal media by means of aqueous solutions is determined by forces of a capillary nature. The capillary forces regulate the reaction velocity, not because they determine the velocity with which the solvent penetrates the colloid particles and moistens their internal surface, but because they control the velocity with which the protein passes from the inside of the colloid particles to the outside solvent. The following relationship between the time and amount of protein dissolved is deduced; $x = kt^m$, in which x is the amount of protein extracted in the time t ; k and m are constants. From the form of the relationship it is clear that although the extraction of the protein is very rapid at first it decreases so rapidly that it cannot be regarded as complete in an experimentally finite time. The above relationship is confirmed by the results of experiments on the rate of extraction of casein by dilute solutions of acids, and the extraction of protamine from the dried spermatozoa of *Oncorhynchus tshawytscha*, Walbaum (*loc. cit.*). J. F. S.

Catalytic Hydrogenisation by Finely Divided Metals. ANTONIO MADINAVEITIA (*Anal. Fis. Quim.*, 1913, 11, 328—333).—Ruthenium and iridium determine the catalytic hydrogenisation of cinnamic acid, but not of toluene, whereas rhodium acts on both substances. Osmium is inactive. G. D. L.

Catalysis. XVII. Reactions of Both the Ions and the Non-ionised Forms of Electrolytes. Reactions of Sodium Phenoxide with Methyl Iodide and Ethyl Iodide in Absolute Ethyl Alcohol at 25° and 35°. H. C. ROBERTSON, jun. and SOLOMON F. ACREE (*Amer. Chem. J.*, 1913, 49, 474—520. Compare Acree, this vol., ii, 576; Marshall, Harrison, and Acree, this vol., ii, 577).—In continuation of the work on catalysis, a study has been made of the velocities of reaction of sodium phenoxide with methyl iodide and with ethyl iodide at 25° and 35° in absolute alcohol at concentrations ranging between N and $N/40$. Constant values have been obtained for K_i and K_m , which represent the velocity of transformation of unit concentrations of phenoxide ions, and of non-ionised sodium phenoxide with alkyl iodides. This is regarded as evidence that both the phenoxide ions and the non-ionised sodium phenoxide react with the non-ionised alkyl iodides, and is supported by the fact that the same value is obtained for K_i with a given alkyl haloid whether the phenoxide ions are derived from the sodium, potassium, or lithium salt. It is probable that the transformation is accompanied by an "abnormal salt effect," and in order to investigate this question it is proposed to determine the reaction velocities in solutions varying in concentration from N to $N/2048$. A similar study has shown that *p*-bromobenzonitrile and sodium, potassium, and lithium ethoxides in solutions ranging

from $N/32$ to $N/2048$ give the same value for K_i for the ethoxide ion in these ideal solutions, but seem to yield different uncorrected values for K_i and K_m in the more concentrated solutions. The abnormal behaviour of the concentrated alcoholic solutions are being investigated by measurements of their fluidities, the effect of added salts on the reaction velocities, and the probable extent of the alcoholation of the reacting constituents.

E. G.

Constitution of Atoms and Molecules. I. N. BOHR (*Phil. Mag.*, 1913, [vi], 26, 1—24).—The author, making use of Rutherford's theory of the constitution of the atom, considers the mechanism by which the revolving electrons are bound to the positive nucleus. The considerations are made in relation to Planck's hypothesis of energy quanta. It is shown that in any molecular system consisting of positive nuclei and electrons in which the nuclei are at rest relatively to each other and the electrons move in circular orbits, the angular momentum of every electron round the centre of its orbit will in the permanent state of the system be equal to $h/2\pi$, where h is the Planck constant.

On the assumption that the hydrogen atom consists of a positive nucleus and a single electron of charge e , the author deduces the expression $v = 2\pi^2 me^4 / h^3 (1/\tau_2^2 - 1/\tau_1^2)$, where m is the mass of an electron, τ_1 and τ_2 are whole numbers, h is the Planck constant, and v is the atomic vibration frequency. This expression accounts for the law connexion of the lines in the hydrogen spectrum. If $\tau_2 = 2$ and τ_1 varies, the expression gives the Balmer series, and if $\tau_2 = 3$ the ultra-red series of Paschen is obtained. If $\tau_2 = 1$ and $\tau_1 = 4, 5$ respectively, series are given in the extreme ultraviolet and infra-red. These have not yet been observed.

J. F. S.

Formation of the Molecules of the Elements and their Compounds with Atoms as Constituted on the Corpuscular-ring Theory. ALBERT C. CREHORE (*Phil. Mag.*, 1913, [vi], 26, 25—84).—The author first describes experiments made to test the corpuscular-ring theory of the atom. A number of steel balls of uniform size are suspended by long, thin copper wires in castor oil and charged to an equal high potential, allowed to take up their equilibrium position, and photographed. In this way it is shown that the arrangement calculated by Thompson is set up, although other equilibria are possible. The radii, etc., for the arrangements which correspond with hydrogen, carbon, nitrogen, oxygen, and fluorine atoms are worked out from measurements made on the photographs of the equilibrium arrangements. The second part of the paper deals with the combination of atoms to form molecules. It is shown that two atoms take up a position of equilibrium to one another in forming a compound, and that there is an attraction between them varying inversely as the fourth power of the distance. The third part of the paper is mathematical, and deals with the calculation of the necessary formulæ involved in the paper.

J. F. S.

Chemical "Lability" and Absorption of Ultraviolet Rays. VICTOR HENRI (*Compt. rend.*, 1913, 156, 1979—1982).—Substances which are chemically labile are said to possess the property of chemical "lability."

An examination of the work which has been done during the past few years leads the author to the following electronic theory of chemical reactions: a substance which reacts readily contains molecules which are able either to liberate or to exchange electrons readily; the linkings between the atoms in a molecule are brought about by the electrons.

Since the absorption of ultraviolet rays is an electronic property, it should follow that compounds which absorb these rays should be chemically labile, and vice versa. An examination of a number of different compounds shows this to be the case. T. S. P.

Reform of Chemical Calculations. C. J. T. HANSEN (*Chem. News*, 1913, 108, 3).—The author has extended the list of atomic weights which are whole numbers (compare A., 1912, ii, 1157) to seventy-six elements. T. S. P.

Piezoechemical Studies. IX. An Automatic Pressure Regulator for High Pressures. ERNST COHEN and R. B. DE BOEK (*Zeitsch. physikal. Chem.*, 1913, 84, 32—40).—The authors describe an automatic apparatus which is capable of regulating the pressure in a reaction bomb to within 1% for pressures up to 1800 atms. This apparatus has been used in the authors' previous work (A., 1909, ii, 291, 641, 796, 857, 981; 1910, ii, 1029; 1911, ii, 23).

J. F. S.

An Automatic Apparatus for the Extraction of Solutions Sensitive to Heat. RICHARD KEMPF (*Chem. Zeit.*, 1913, 37, 774).—The solution to be extracted is contained in a jacketed glass tube, which can be cooled by a current of cold water. Into this glass tube is fitted, at the top, a reflux condenser, and between the lower end of the condenser and upper end of the jacket are sealed two side-tubes, the lower one of which leads to the bottom of a flask containing the extracting liquid, and serves as an overflow for this liquid from the jacketed tube. The upper side-tube serves to conduct the vapour from the flask to the reflux condenser. Just below the end of the condenser is a funnel which is sealed on to a spiral of glass tubing which reaches to the bottom of the jacketed tube. The liquid from the condenser runs down through this spiral, and is forced, by hydrostatic pressure, up through the solution to be extracted, and overflows into the above-mentioned flask. T. S. P.

A New Form of Condenser. RICHARD ASCHER (*Zeitsch. angew. Chem.*, 1913, 26, 408).—To avoid the instability caused by the introduction of an adapter between a condenser and the flask of boiling liquid the author constructs the inner tube of the condenser with a short T-piece at one end, making an angle of 60° with the cooling

portion of the tube. The two short arms of the T-piece can be fitted to a flask, and with a thermometer or tap-funnel respectively. When the condenser is so disposed that the smaller angle of the T-piece is below, it is in position for ordinary distillation, whilst when turned with the smaller angle above it is ready for refluxing.

D. F. T.

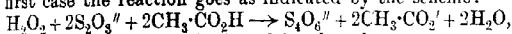
A New Modification of the Liebig Reflux Condenser. WALTHER FRIESE (*Pharm. Zentr.h.*, 1913, 54, 670).—The ordinary condenser, in which the inner tube is expanded into a series of bulbs, is modified in such a way that the cooling area of the bulbs is increased by making the upper and lower end of each bulb re-entrant (as the lower end is in the head of an alembic). In order to prevent the condensed liquid collecting in the bottom channel thus formed in each bulb, a tube is sealed into the lowest part and connected with the top portion of the next lower bulb.

T. S. P.

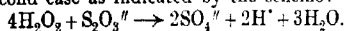
The L-Condenser. KARL LÜDECKE (*Chem. Zeit.*, 1913, 37, 838).—A condenser has already been described by the author (*ibid.*, 1905, 29, 1282) in which condensation is effected by internal cooling with an inner tube enlarged into a series of bulbs; it can be used over a water-bath without condensing the steam and so wetting the cork of the flask. The condenser is very effective, and the earlier disadvantage that a little of the condensed liquid in distillations was retained in the lower portion of the condenser is now obviated by attaching the inlet and outlet tubes for the vapour and condensed liquid in a line with the side of the condenser instead of centrally.

D. F. T.

Lecture Experiment to Show the Specific Action of Catalysts. EMIL ABEL (*Zeitsch. Elektrochem.*, 1913, 19, 480—482. Compare A., 1908, ii, 26; 1912, ii, 927).—The author has shown (*loc. cit.*) that the reaction between hydrogen peroxide and thiosulphate is catalysed differently by iodine and molybdic acid. In the first case the reaction goes as indicated by the scheme:



and in the second case as indicated by the scheme:



If both reactions are started and a little barium chloride solution added to each, in the first case there will hardly be a cloudiness, whilst in the second a continuous formation of sulphate will occur. Further, if a drop of hydrochloric acid is added to each reaction and then a drop of methyl-orange solution which is just acid, in the first case the colour will change to yellow as the reaction proceeds, whilst in the second case it will become notably redder. As is visible from the equations, the end of the reaction in the first case is conditioned by the using up of all the thiosulphate, and in the second case by the using up of the hydrogen peroxide. Consequently there is an excess of hydrogen peroxide over thiosulphate in the first case, and vice versa in the second case. This is shown by

adding starch to the first reaction, when a deep blue colour will be formed due to the iodine liberated by the action of the H_2O_2 on the sodium iodide formed in the reaction. In the second case even on adding potassium iodide there is no blue colour formed in the presence of starch, showing the absence of hydrogen peroxide. As a lecture experiment the author recommends the following quantities. The volume of the reaction mixture in each case should be 100 c.c., made up of (I) $0.1\text{N}\text{H}_2\text{O}_2$, $0.025\text{N}\text{Na}_2\text{S}_2\text{O}_3$,

$0.025\text{N}\text{CH}_3\cdot\text{CO}_2\text{H}$,

a little $0.025\text{N}\text{BaCl}_2$ and $0.004\text{N}\text{HCl}$, a few drops of methyl-orange, and a little starch and $0.25\text{N}\text{KI}$; (II) as (I) except that the $0.25\text{N}\text{KI}$ is replaced by 0.0002 mol. Na_2MoO_4 . The reaction is complete in a few minutes, and the changes indicated can all be observed.

J. F. S.

Two Lecture Experiments. [Preparation of (I) Copper Acetylide, (II) the ψ -Nitrole of Nitroisopropane.] HANS RUPE (*J. pr. Chem.*, 1913, [ii], 88, 79—82).—Details are given of the preparation of copper acetylide and the methods adopted to show its explosive character when brought in contact with nitric acid, potassium permanganate and sulphuric acid, bromine, and chlorine.

The second experiment illustrates the formation of the ψ -nitrole of nitroisopropane by passing nitrous gases from arsenious oxide and nitric acid into a concentrated ethereal solution of acetoxime. The formation of the ψ -nitrole may be more readily shown in the following manner: An aqueous solution of acetoxime and sodium nitrite is covered with ether, and dilute hydrochloric acid added drop by drop with constant shaking, when the ether rapidly acquires a deep blue colour.

F. B.

A Modified Borman's Gas-generating Apparatus. J. MAREK (*Zeitsch. anal. Chem.*, 1913, 52, 419—421).—An improved form of the apparatus described and figured by Borman (*A.*, 1912, ii, 931).

L. DE K.

Inorganic Chemistry.

Bromides. IV. ICHIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1912—1913, 48, 735—749. Compare this vol., ii, 333).—The author has continued his investigation of the stability of bromides with the aid of the test previously described. The paper also contains information regarding the hydrates of the salts described.

Anhydrous lithium bromide evolves bromine when heated to its m. p., and also (in small quantity) when it is boiled with water and iodine. Ammonium bromide sublimes and dissociates on heating, but does not yield bromine. Sodium bromide does not evolve bromine (or only traces) when heated even above its m. p.

Bromine is rapidly eliminated, however, when the salt is heated with excess of iodine. Rubidium bromide loses bromine above its m. p., but only gives the smallest trace of bromine when heated with water and iodine. If the dry salt is heated with iodine, however, much bromine is evolved. Cæsium bromide does not yield bromine on heating, and only gives traces with water and iodine; with iodine in the absence of water, however, bromine is evolved even at the ordinary temperature, and on heating the evolution is very considerable. Thallium bromide does not lose bromine even at high temperatures; it is more stable than the bromides of potassium and sodium. When it is heated with iodine, bromine is evolved. Silver bromide behaves similarly. All the above-mentioned bromides yield bromine when heated with chromic acid.

The action of chromic acid on silver bromide may be used to detect traces of this salt, even in presence of other silver haloids. In the reaction, oxygen and bromine are evolved, and metallic silver and chromium sesquioxide are formed.

Mercurous bromide sublimes when heated, and during the sublimation no bromine is liberated. The salt yields bromine, however, when rapidly heated with excess of iodine or with very concentrated chromic acid. Iodine reacts with mercurous bromide even at the ordinary temperature, and a mixture of mercuric iodide and mercuric bromide is formed. This reaction agrees with Werner's formula, $\text{Hg} \cdot \text{Hg} \cdot \text{Br}_2$, for mercurous bromide.

Anhydrous cuprous bromide evolves bromine at its m. p. The salt also yields bromine when heated with 25% chromic acid.

R. V. S.

The Existence of Bromites. J. CLARENS (*Compt. rend.*, 1913, 156, 1998—2000).—A fresh solution of hypobromite, made by the solution of bromine vapour in a solution of potassium or sodium hydroxide, was divided into two parts; the one was treated with an excess of ammonium chloride, whilst the other was first heated at 80° for a few minutes, and then excess of ammonium chloride added. The first solution was without action on an alkaline arsenite solution in the cold, whilst the second oxidised it, the oxidising power being as much as one-tenth of that originally possessed by the hypobromite solution. The oxidising agent still present in the second solution could not be bromate, since bromate does not oxidise an arsenite in cold alkaline solution; it was probably bromite. This was proved to be the case by analysis, as follows. The hypobromite present in the (second) solution was destroyed with carbamide, and the bromide precipitated as silver bromide. After collecting the precipitate, the filtrate was divided into three portions, which were analysed as follows: In the first portion the oxidising power towards a cold alkaline arsenite solution was determined; in the second portion the oxidising power towards a cold, strongly acid arsenite solution was measured; the third portion was evaporated to dryness, the residue calcined to destroy bromate and bromite, and the amount of bromide estimated. The results of these three analyses gave the formula, MBro_2 , that is, that

of a bromite, as the oxidising substance present in the second solution.

T. S. P.

The Oxidation of Some Inorganic Substances at High Pressures and Temperatures. JAROSLAV MILBAUER (*Eighth Inter. Cong. App. Chem.*, 1912, 2, 183—185).—The action of oxygen at 480° and a pressure of 12 atmospheres on various oxides and mixtures of oxides has been investigated. The oxides of the following metals give peroxides: lithium, sodium, potassium, and barium. A small proportion of higher oxides is given by the oxides of cobalt and nickel. Lead oxide gives red lead, antimony oxide gives the tetroxide, and chromium sesquioxide gives chromium chromate. The oxides of the following metals and elements remain unaltered: glucinum, calcium, strontium, zinc, cadmium, aluminium, boron, thallium, silicon, zirconium, tin, bismuth, molybdenum, tungsten, uranium, and iron.

The two-component mixtures investigated all contained chromium oxide as the one component; all of them, with the exception of the mixture with cerium oxide, gave chromates. In the second column of the periodic system the amount of oxygen absorbed diminishes in the inverse ratio of the atomic weight of the metal.

T. S. P.

The Action of Carbon Dioxide on the Mineral Sulphides. N. D. COSTEANU (*Compt. rend.*, 1913, 156, 1985—1987).—The action of carbon dioxide on sulphides, at temperatures below that at which dissociation of the carbon dioxide takes place, has been studied.

Silver, copper, cadmium, bismuth, and antimony sulphides were not acted on. Silicon sulphide reacted slowly at 1100° in accordance with the equation: $2\text{CO}_2 + \text{SiS}_2 = 2\text{CO} + 2\text{S} + \text{SiO}_2$; the same reaction takes place even at 450°. The results show, at the same time, that carbon dioxide has no action on sulphur at these temperatures.

T. S. P.

Colloidal Selenium. ALEXANDER GUTBIER and FR. HEINRICH (*Koll. Chem. Beihefte*, 1913, 4, 411—457).—The authors have studied the reduction of selenious acid to selenium by means of a series of reducing agents, and also the reversibility of the disperse selenium system produced in these actions. It is shown that in the reduction of selenious acid solution by sulphurous acid the maximum reduction occurs when the substances are present in the molecular relationship $1\text{SeO}_2 : 2\text{SO}_2$. The colour of the solutions in the above case is reddish-yellow when the selenium oxide is above the given relationship, and changes toward the green with an excess of sulphur dioxide. The colour is in this sense dependent on the way the liquids are mixed. When solutions of selenium dioxide are reduced by sodium or ammonium hydrogen sulphite, a maximum reducing action is found to occur at the molecular relationships $1\text{SeO}_2 : 2.5$ — 2.7NaHSO_3 and $1\text{SeO}_2 : 1.8$ — $2.0\text{NH}_4\text{HSO}_3$. Just as in the reductions by sulphur dioxide the colour of the

solutions tends towards the green in the presence of the reducing agent. All these reductions take place in the absence of hydrochloric acid. Reduction with sodium hyposulphite ($\text{Na}_2\text{S}_2\text{O}_4$) occurs very rapidly, the velocity increasing with the increasing amount of the reducing agent, and decreasing with increasing dilution of the solution. A maximum reduction relationship could not be observed. A relationship appears to exist between the velocity of sedimentation and the concentration of the hyposulphite, in the sense that sedimentation is more rapid the greater the concentration of hyposulphite. In those cases where there is a large concentration of hyposulphite, the deposited red selenium often changes into the black modification when kept. Hydrazine hydrate reduces solutions of selenious acid very rapidly, but no maximum reduction relationship could be observed, and the coagulation of the selenium sols occurred at about the same time with all quantities of the reducing agent. Hydrazine chloride and sulphate behave exactly like the hydrate. The relative velocity of reduction of the substances investigated is shown to be in the following order: sodium hyposulphite, hydrazine chloride, sulphurous acid, hydrazine sulphate, and hydrazine hydrate. The selenium obtained by reduction with sulphurous acid dissolves in water to form a colloidal solution, and the red disperse system so formed, which can be filtered without a residue, coagulates extremely slowly. During sedimentation, it forms two layers, the upper one being bluish-red to yellowish-green, and the under one turbid red. A solid hydrosol of selenium can be obtained by evaporation of the above-mentioned solution in a vacuum. This is a reddish-brown powder, which partly dissolves in water to form a yellowish-green solution, and a turbid red sol can be formed by rubbing the residue with water. Selenium prepared by reduction with sodium or ammonium hydrogen sulphite forms colloidal solutions, that precipitated by the sodium salt passing more easily into solution than that precipitated by the ammonium salt. Reduction with sodium hyposulphite produces reversible and stable sols so long as the relationship $1\text{SeO}_2 : 2-2.8\text{Na}_2\text{S}_2\text{O}_4$ is not exceeded in the reduction. Selenium produced by hydrazine hydrate or the hydrazine salts is completely irreversible.

J. F. S.

The Atomic Weight of Tellurium; and a Critique of the Basic Nitrate Method of Determination. WILLIAM L. DUDLEY and PAUL C. BOWERS (*J. Amer. Chem. Soc.*, 1913, 35, 875-880).—A continuation of the earlier investigation (Dudley and Jones, A., 1912, ii, 935). Tellurium, which had been purified in the manner described earlier, was dissolved in nitric acid for the purpose of determining the atomic weight by the basic nitrate method, but it was found to separate, on crystallisation, sometimes as orthorhombic basic nitrate, and sometimes as octahedral dioxide; the latter could be converted into basic nitrate by further treatment (repeatedly if necessary) with nitric acid. The figures calculated from the results of the decomposition of the basic nitrate were, however, so irregular that the method was abandoned. Tellurium

may crystallise from nitric acid solution as tellurous acid, tellurium dioxide, and basic nitrate, and the exact conditions for the separation of pure crystals of any one appear to be very elusive.

In the failure of the basic nitrate method, the tetrabromide method was applied to the determination of the atomic weight of the various fractions of the tellurium precipitated by hydrazine hydrochloride, and also of the element in the various specimens of basic nitrate obtained above. The results indicate the identity of the tellurium in every case.

D. F. T.

Effect of Free Chlorine on the Product of Hydrolysis of Tellurous Chloride. PHILIP E. BROWNING and GEORGE O. OVERHELMAN (*Eighth. Inter. Cong. App. Chem.*, 1912, 2, 59-62).—In Harcourt and Baker's discussion (T., 1911, 99, 1311) of the work of Browning and Flint on the hydrolysis of tellurous chloride, they state that the yellow colour sometimes observed in the hydrolytic fractions was found by them to be due to a small amount of telluric oxide present in their material, presumably because of chlorine set free from the hydrochloric acid by the action of bright sunlight. The authors find that if pure tellurous oxide is dissolved in hydrochloric acid which has been exposed to bright sunlight, the solution hydrolysed with boiling water, and the precipitate thus formed boiled with pure hydrochloric acid, no chlorine is liberated. Moreover, if the solution of tellurous oxide in hydrochloric acid is saturated with chlorine both before and after hydrolysis, the amount of chlorine liberated when the precipitate is boiled with hydrochloric acid is very small, the amount of tellurium trioxide formed being less than 0.5%.

It follows that the results obtained by Browning and Flint cannot be due to an error caused in the way suggested by Harcourt and Baker.

T. S. P.

An Active Modification of Nitrogen Produced by the Electric Discharge. V. (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1913, A, 88, 539-549. Compare A., 1911, ii, 482; 1912, ii, 153, 477, 935).—An improved method is described for preparing and storing pure nitrogen containing less than 1/150,000 of its volume of oxygen. It is shown that, despite criticisms, the presence of traces of oxygen in the nitrogen used is not essential or even favourable to the formation of active nitrogen. The addition of oxygen hinders the formation, 2% preventing the action altogether. Hydrogen and carbon dioxide as impurities have but little effect on the action, but traces of water vapour are decidedly harmful. Nitrides are formed by passing active nitrogen into vapours of mercury, cadmium, zinc, arsenic, sodium, and sulphur. These nitrides are decomposed by water or potassium hydroxide, giving ammonia. Carbon disulphide yields a blue, polymeric nitrogen sulphide and a polymeric carbon monosulphide. Sulphur chloride gives ordinary yellow nitrogen sulphide. Stannic chloride and titanium chloride also yield solid products; in the latter case nitro-

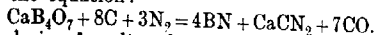
gen was shown to be present. The following compounds give hydrogen cyanide when treated with active nitrogen: acetylene, benzene, pentane, methyl bromide, ethyl iodide, ethyl chloride, chloroform, ethylene dichloride, ethylidene dichloride, and ether. Carbon tetrachloride and carbon disulphide gave no trace. When chlorine is present, cyanogen chloride is produced, and benzene also gave cyanobenzene. The intensity of the cyanogen spectrum with organic compounds is no index of the quantity of hydrogen cyanide being formed. Preponderance of the real cyanogen bands is associated with cyanogen chloride and bromide. Generally there does not appear to be any definite connection between the development of spectra by active nitrogen and the chemical actions in progress.

J. F. S.

Fixation of Atmospheric Nitrogen by means of Boron Compounds. I. Decompositions under High Pressures.

ARTHUR STÄHLER and JOHN JACOB ELBERT (*Ber.*, 1913, 46, 2060—2077).—The object of the authors' experiments was to determine the conditions under which boron nitride may best be obtained from naturally occurring compounds of boron. Since in such compounds the boron is generally combined with oxygen, it was necessary to investigate first the best methods for their reduction, and then the combination with nitrogen of the boron or boride formed.

The reduction of boron trioxide by carbon begins to take place at 1200°; in the presence of nitrogen, calcium borate (borocalcite) undergoes reduction at 1280°, reaction probably taking place according to the equation:



The electrolysis of molten borax gave yields of boron to the extent of 12.1%. Carbon electrodes were first used, but they broke off repeatedly at the surface of the fusion; iron electrodes lasted longer, but they also broke off after a time.

Attempts to reduce boron trioxide by means of calcium carbide at 1625° made it probable that the product of reaction was calcium boride, which has previously been prepared by Moissan.

Before carrying out further experiments on the production of boron nitride it was necessary to determine its stability; it was found that decomposition with evolution of nitrogen only commenced to take place at 2450°; this temperature of decomposition holds only in the presence of carbon, since the boron nitride was contained in a graphite crucible.

The next experiments were confined to mixtures of carbon with either boron trioxide or borocalcite. These were heated to different temperatures in an atmosphere of nitrogen under different pressures, a special electrical furnace having been constructed in which reactions could be carried out at pressures up to 500 kg. per sq. cm., and at temperatures up to 2500°.

With mixtures of boron trioxide and carbon and nitrogen at atmospheric pressure, the best yield, 26—28%, of boron nitride is obtained between 1500° and 1700°. With increasing pressure

the yield increases, more than 85% of boron nitride being obtained at a pressure of 70 kg. per sq. cm. and a temperature of 1600° . When the boron trioxide is replaced by borocalcite, a nearly theoretical yield of boron nitride, according to the equation given above, is obtained when the temperature is maintained at 1850° for thirty minutes and 1400° for fifteen minutes; increase in pressure of the nitrogen has no effect on the yield. At normal pressures the amount of nitrogen absorbed per gram of boron is much greater with borocalcite than with boron trioxide; only at very high pressures are better results obtained with boron trioxide than with borocalcite.

T. S. P.

Catalytic Action of Iodine. MORITZ KOHN and ALFONS OSTERSETZER (*Zeitsch. anorg. Chem.*, 1913, 82, 240—241).—The reaction between phosphorus trichloride and sulphur chloride, $3\text{PCl}_3 + \text{S}_2\text{Cl}_2 = \text{PCl}_5 + 2\text{PSCl}_3$, is accelerated by iodine, and a yield of 88% of phosphorus pentachloride may be obtained.

C. H. D.

The Retention of Small Quantities of Water by Arsenic Pentoxide at Elevated Temperatures. ALAN W. C. MENZIES and PAUL D. POTTER (*Eighth. Inter. Cong. App. Chem.*, 1912, 2, 179—182).—An investigation of the amount of water lost by the hydrate, $3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$, when heated for different lengths of time at different temperatures in a current of dry air or of air of known humidity.

T. S. P.

Total Adsorption of Arsenious Oxide by Ferric Hydroxide. GEORG LOCKEMANN and FRANZ LUCIUS (*Zeitsch. physikal. Chem.*, 1913, 83, 735—758. Compare A., 1911, ii, 485, 720).—A continuation of the work of Lockemann and Paucke, in which the quantity of iron hydroxide required for the total adsorption of arsenious oxide is determined at a series of temperatures, the iron always being exactly precipitated by the theoretical quantity of ammonia. The influence of sodium and ammonium salts in the formation of soluble basic iron salts is examined, and it is shown that sodium nitrate has the least tendency to form such salts, and ammonium sulphate the greatest. It is then shown that in the presence of salts it is better to add the ammonia to the iron salt in two portions; thus, if one-third the required amount of ammonia is added, and then after fifteen minutes the residue, the total adsorption is more regular and reproducible than if other conditions are adopted. The adsorption occurs less perfectly at higher temperatures than at lower temperatures, and the difference in the adsorption is more marked at lower concentrations than at higher. Thus, at 40° , the quantity of iron hydroxide required for the total adsorption of 0.1 mg. arsenic in 100 c.c. is three times as much as is required at 0° , and at 80° six times as much is required; but for the total adsorption of 300 mg. per 100 c.c., the amounts at 40° and 80° are only one and a-half and two and a-half times respectively the quantity required at 0° . The total adsorption of arsenic by ferric hydroxide follows the formula $E = \beta AP$, in which E represents the

number of mg. of iron hydroxide, A the number of mg. arsenic per 100 c.c., and β and p are constants, which differ for different temperatures. The total adsorption of arsenic is not materially influenced by the presence of sodium and ammonium salts. The precipitation of arsenic by iron hydroxide is a usable process for the purification of concentrated salt solutions, and for the detection of small traces of arsenic in solutions or nitre fusions. J. F. S.

Boron Hydrides. II. A New Boron Hydride, B_2H_6 . Carbon Disulphide Cooling Bath for Maintaining a Constant Temperature of -112° . ALFRED STOCK and KURT FRIEDERICI (*Ber.*, 1913, **46**, 1959—1971).—When the boron hydride, B_4H_{10} (compare Stock and Massenez, this vol., ii, 44), is preserved at room temperature over mercury, it slowly undergoes decomposition, with the formation of a new boron hydride, B_2H_6 , the only other gaseous product of decomposition being hydrogen. The decomposition is not appreciably affected by sunlight, but is accelerated to a great extent by ultra-violet light. At 100° the decomposition is complete in a few hours, whereas at ordinary temperature it takes a month or more.

The composition, B_2H_6 , of the new hydride was proved (1) by decomposition with water, which is very rapid, and takes place quantitatively according to the equation: $B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$, (2) by explosion with excess of air, (3) by determination of the density, which gave a molecular weight of 27.8 (theory for B_2H_6 , 28.0).

B_2H_6 is a colourless gas possessing a characteristic, repulsive odour, resembling that of the hydride B_4H_{10} , and to some extent that of hydrogen sulphide. The vapour tensions at the following temperatures, -130° , -120° , -112.1° , -110° , -100° , and -90° , are respectively 4, 10, 22.4, 25, 40, and 65 cm.; the b. p. is -87° to $-88^\circ/760$ mm., and the m. p. $< -140^\circ$. It is much more stable than B_4H_{10} , but nevertheless decomposes very slowly at ordinary temperatures. When submitted to the action of electrical sparks boron is deposited, and non-volatile boron hydrides of objectionable odour formed. When heated with the bare flame, colourless and yellow solid hydrides are formed, but no liquid products, as is the case with the hydride B_4H_{10} ; the chief product crystallises in long, colourless needles, which are not decomposed by water, and dissolve in sodium hydroxide.

B_2H_6 only takes fire in the air when mixed with other boron hydrides. With alkalis, it reacts similarly to B_4H_{10} ; for example, with sodium hydroxide it gives solutions in which the presence of hypoborates must be assumed. B_4H_{10} is at first completely absorbed by sodium hydroxide (*loc. cit.*), but B_2H_6 gives some hydrogen immediately it comes in contact with the alkali.

The formula B_2H_6 shows that boron must be at least quadrivalent, and not trivalent as a maximum, as it should be according to its position in the periodic system.

A carbon disulphide cooling bath for maintaining a constant

temperature of -112° is described. It was used in fractionating the decomposition products of the hydride B_4H_{10} . T. S. P.

Borates. System $CaO-B_2O_3-H_2O$ at 30° . II. UMBERTO SBOGRI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 715—719).—The paper gives the numerical results of the author's experiments, a discussion of which is to follow. R. V. S.

Composition of the Gaseous Mixtures Resulting from the Action of Water on the Carbides of Uranium and Thorium. PAUL LEBEAU and A. DAMIENS (*Compt. rend.*, 1913, 156, 1987—1989).—The gas evolved by the action of water on the carbides of uranium and thorium is proved to be a mixture of the following: hydrogen, methane, ethane, propane, butane, ethylene, propylene, and homologues, acetylenic hydrocarbons. Uranium carbide reacts very slowly, the reaction lasting from five to twenty-five days or longer; thorium carbide reacts much more quickly, three to four days.

Two specimens of uranium carbide were used, one containing 1.47% of graphite and the other free from graphite. The reaction is much slower with the latter carbide, and the gases are more completely hydrogenised, as shown by the fact that the proportion of hydrogen diminishes, whilst that of the hydrocarbons, especially methane, propane, butane, and propylene, increases.

The gases were analysed by the method previously described (this vol., ii, 349). T. S. P.

The Composition of Water Gas. LÉO VIGNON (*Compt. rend.*, 1913, 156, 1995—1998).—The author confirms the observation of Clément and Désormes and of Langlois that water-gas always contains some methane. Further investigation has shown that the formation of the methane is due to the presence of calcium oxide in the coke used. Experiments on the action of steam at 1000° on mixtures of coke and lime showed that the percentage of methane in the water-gas increased with increasing proportions of lime. The formation of the methane is considered to be due to the following reactions: $4CO + 2H_2O = 3CO_2 + CH_4$; $2CO + 2H_2 = CO_2 + CH_4$; $CO_2 + 4H_2 = CH_4 + 2H_2O$. The lime acts as a catalyst on these reactions. T. S. P.

Mixed Crystals of Potassium and Ammonium Chlorides. KENJIRO UYEDA (*Mem. Coll. Sci. Eng. Kyoto*, 1913, 5, 147—150).—The author has determined the mutual solubilities of potassium and ammonium chlorides at 25° , 65° , and 90° respectively. The mutual solubilities increase with rise in temperature, the increase in the case of ammonium chloride in potassium chloride being much more rapid than in the case of potassium chloride in ammonium chloride. The gaps in the series of mixed crystals lie between the following molar percentages of ammonium chloride: 27—95% at 25° , 46—93% at 65° , and 69—90% at 90° . T. S. P.

The Reduction of Some Metallic Chlorides by Sodium. MATTHEW A. HUNTER (*Eighth. Inter. Cong. App. Chem.*, 1912, 2, 125—138).—The author has constructed a special steel bomb, capable of withstanding high pressures, in which the action of sodium on various chlorides at high temperatures could be studied. In such an apparatus titanium tetrachloride is readily reduced by sodium; if the amount of material used is great enough, the heat of reaction is sufficient to give the titanium metal in a coherent condition.

Both carbon tetrachloride and carbon disulphide can be reduced by sodium, the temperature and pressure produced during the reaction being considerable. There is no conclusive evidence that fusion of any part of the material takes place during the reaction. A crystalline residue, microscopic in amount, appears to possess some of the properties of crystalline carbon. Some sodium carbide is formed as a by-product of both reactions, and if too little sodium is present for complete reduction of the carbon tetrachloride, some carbon hexachloride is produced.

Glucinum chloride gives glucinum metal, the properties of which are to be investigated further.

Silicon tetrachloride is reduced with difficulty, giving finely-divided silicon. Great difficulty was experienced in maintaining the bomb air-tight.

Neodymium chloride gives finely-divided neodymium, which is not readily separated from the sodium chloride produced during the reaction.

T. S. P.

Equilibria in the Systems: Water, Sodium Nitrite and Water, Sodium Nitrite and Sodium Nitrate. MARCEL OSWALD (*Eighth. Inter. Cong. App. Chem.*, 1912, 2, 205—207).—The author has determined the solubility curve of sodium nitrite, and also the mutual solubilities of sodium nitrate and nitrite at different temperatures.

Sodium nitrite does not give a stable hydrate. Sodium nitrite and nitrate form neither a double salt nor mixed crystals.

T. S. P.

Disodium Monohydrogen Phosphate and its Hydrates. Their Solubilities and Transition Temperatures. ALAN W. C. MENZIES and EDMUND C. HUMPHREY (*Eighth. Inter. Cong. App. Chem.*, 1912, 2, 175—178).—The determination of the solubility curve of disodium hydrogen phosphate has given the following transition temperatures: dodecahydrate to heptahydrate, 35.2°; heptahydrate to dihydrate, 48.3°; dihydrate to anhydrous salt, 95°. The euhydric temperature is -5°. The solubility of the anhydrous salt diminishes with rise in temperature.

T. S. P.

Equilibrium of Lithium Sulphate with the Alkali Sulphates in their Mixed Solutions up to 100°. (Mlle.) CÉCILE SPIELREIN (*Compt. rend.*, 1913, 157, 46—48. Compare A., 1912, ii, 917).—A continuation of the study of the solubility of lithium sulphate in

water in the presence of alkali sulphates up to 100°. The results show the existence of several double salts. With sodium sulphate it gives salts: $\text{Li}_2\text{SO}_4, \text{Na}_2\text{SO}_4, 5\frac{1}{2}\text{H}_2\text{O}$ at 0°, which ceases to exist at 16°; $\text{Li}_2\text{SO}_4, 3\text{Na}_2\text{SO}_4, 12\frac{1}{2}\text{H}_2\text{O}$ from 16–24°; $4\text{Li}_2\text{SO}_4, \text{Na}_2\text{SO}_4, 5\text{H}_2\text{O}$ at 28°, and between 32° and 100° $\text{Li}_2\text{SO}_4, \text{Na}_2\text{SO}_4, 3\text{H}_2\text{O}$. With potassium sulphate it forms one double salt, $\text{Li}_2\text{SO}_4, \text{K}_2\text{SO}_4$, and with ammonium sulphate one double salt, $\text{Li}_2\text{SO}_4, (\text{NH}_4)_2\text{SO}_4$, up to 100°.

W. G.

Forms of Silver. Physico-chemical Morphology. VOLKMAR KOHLSCHÜTTER (*Zeitsch. Chem. Ind. Kolloid*, 1913, 12, 285–296).—A theoretical paper, in which the relationships between the various forms of silver are discussed. The material contained in the paper has all been previously published (compare A., 1908, ii, 182; 1912, ii, 253, 731, 845; this vol., ii, 285, 286, 287).

J. F. S.

Silver Oxide. H. VON WARTENBERG (*Zeitsch. Elektrochem.*, 1913, 19, 489–491).—The author shows that silver vapourises more easily in oxygen than in nitrogen, which he explains by the formation of an oxide, probably Ag_2O . The stability of the oxide is explained from its large heat of vaporisation, which lies probably between –90.6 and –109 Cal. If silver vapour in oxygen is rapidly cooled traces of oxide can be detected in the condensed material.

J. F. S.

Action of Light on Silver, Mercurous, Lead and Cuprous Azoimides; Basic Azoimides of Lead and Copper. LOTHAR WÖHLER and W. KRUPKO (*Ber.*, 1913, 46, 2045–2057).—With the object of gaining further insight into the chemical condition of the photographic latent image, the authors have studied the action of light on the above azoimides. They find that decomposition occurs with immediate formation of the metal, and not of a sub-compound. Hence, by analogy, they are led to the conclusion that the photochemical alteration in the silver haloid of a photographic plate is due to an adsorption compound of finely-divided metal with unchanged haloid, and not to various subhaloids of different colours.

Silver azoimide is highly sensitive to light, decomposition occurring with evolution of nitrogen. In a specimen which had been exposed to light for such a period that decomposition had not occurred beyond the stage corresponding with the possible formation of a sub-azoimide, particles of metallic silver were visible under the microscope, and the residue behaved, when heated or subjected to percussion, in the same manner as silver azoimide. Full details of the precautions necessary in performing these tests are recorded.

Mercurous azoimide is more sensitive to light than the corresponding silver compound. In this case decomposition does not follow the same course as with calomel and other mercurous compounds, since mercuric azoimide is not formed. The percussion test points to immediate decomposition into mercury and nitrogen, and

the non-formation of a sub-azoimide is further confirmed by the absence of hydrazoic acid from the products of the decomposition of mercurous azoimide suspended in water.

Lead azoimide, which is extremely sensitive to light, decomposes according to percussion and temperature tests into metallic lead and nitrogen when the dry salt is illuminated. When exposed to air or placed under water, oxidation of the separated lead proceeds simultaneously, and the product consists of basic lead azoimide mixed with finely-divided lead hydroxide. The filtrate contains traces of lead, hydrazoic acid, and considerable quantities of ammonia. Reaction thus appears to proceed simultaneously according to the three equations: (i) $\text{PbN}_6 + 2\text{H}_2\text{O} = \text{Pb}(\text{OH})_2 + 2\text{N}_3\text{H}$; (ii) $\text{PbN}_6(\text{in light}) = \text{Pb} + 3\text{N}_2$; (iii) $\text{Pb} + \text{N}_3\text{H} + 2\text{H}_2\text{O} = \text{Pb}(\text{OH})_2 + \text{N}_2 + \text{NH}_3$. When preserved in the dark, lead azoimide is practically unaltered after twenty-four hours at 115° .

Cuprous azoimide, CuN_3 , is obtained by the gradual addition of a solution of sodium azoimide to excess of a concentrated solution of copper sulphite to which potassium sulphite has been previously added, followed by acetic acid in quantity just sufficient to dissolve the precipitate formed. It forms a pale greenish-grey precipitate, which inflames at 220° . When exposed to light, it becomes deep red with a violet tint, and decomposes into copper and nitrogen.

Basic lead azoimide, PbO, PbN_6 , has been prepared by three methods: (i) by heating the calculated quantities of lead azoimide and lead hydroxide under water in a sealed tube at 140° for twelve to fifteen hours, and separation of the basic azoimide from specifically heavier unchanged azoimide by elutriation. The method has the drawback that large spontaneously explosive crystals of lead azoimide are liable to separate during the slow cooling of the tube; (ii) by leading a current of carbon dioxide-free air through a boiling aqueous suspension of lead azoimide until the calculated amount of hydrazoic acid has been evolved; and (iii) by heating the requisite quantities of freshly precipitated lead hydroxide and lead azoimide under water on the water-bath for twenty hours. The two latter methods yield uniform products. The basic azoimide is less sensitive to percussion or temperature than lead azoimide, whilst an intimate mixture of lead azoimide and oxide in the proportions necessary to form the sub-azoimide shows the same sensitiveness as the pure azoimide. It is interesting to note that lead azoimide when mixed with 30% water has the same sensitiveness as the dry azoimide, whilst moist mercurous azoimide is scarcely less sensitive than the dry product.

Basic cupric azoimide, CuO, CuN_6 , is obtained as a yellow substance which retains water when a suspension of the normal azoimide in water is heated at $70\text{--}80^\circ$ in a current of air free from carbon dioxide until the calculated quantity of hydrazoic acid has been evolved. It inflames at 245° . When, however, cupric azoimide and cupric hydroxide are warmed under water, hydrazoic acid is evolved and cupric hydroxide alone remains.

Basic mercuric azoimide is not obtained when a solution of free hydrazoic acid is warmed with excess of mercuric oxide, whilst

mercuric azoimide is unchanged when air is passed through a suspension of it in water.

A series of experiments is described on the connexion between the size of crystals and the tendency towards spontaneous detonation, from which it appears that the size of the crystals has a far more pronounced influence on the percussion test than on the temperature test.

H. W.

The Coupling of Metallic Silver and Copper with the Arsenic Haloids. SIEGFRIED HILPERT and FRITZ HERRMANN (*Ber.*, 1913, **46**, 2218—2225).—When molecular silver, prepared either by the action of hydrazine sulphate on an ammoniacal silver nitrate solution or by the reduction of silver chloride with zinc, is well shaken in a sealed tube with molten arsenic tribromide, combination takes place with the formation of a *silver arsenic bromide*, Ag_3AsBr_3 , which is readily freed from the excess of arsenic tribromide by washing with ether. After drying in a vacuum over phosphoric oxide, it forms an amorphous, black, odourless powder. That it is a chemical individual is shown by the following reactions: Cold water has very little action in the cold, but in the warm, grey, metallic silver is formed; this decomposition takes place readily in the cold with ammonium or potassium hydroxides. That the arsenic is directly linked with the bromine in the compound is shown by the fact that magnesium phenyl bromide gives a 70% yield of triphenylarsine. When the substance is digested with a concentrated solution of potassium cyanide, fission takes place in such a way that free arsenic is produced, the silver going into solution as a complex silver salt. A control experiment showed that molecular silver, potassium, cyanide, and arsenious acid react very slowly, giving arsenic, but this reaction could not account for the previous one. The compound is very stable, arsenic being volatilised only at a dark red heat. It is considered to have

the constitution $\begin{array}{c} \text{Ag} \diagup \\ \text{Ag} \diagdown \end{array} \text{As} \begin{array}{c} \diagup \text{Br} \\ \diagdown \text{Br} \end{array}$, the arsenic atom possessing the co-ordination number 6.

When arsenic trichloride is used instead of the tribromide, a *compound* is obtained which is similar in its properties to the silver arsenic bromide described. It has, however, the composition $7\text{Ag}_2\text{AsCl}_3$; with potassium cyanide a substance of the composition AgAs_3 is obtained (it is not certain whether this is a definite compound), as well as arsenic, which seems to indicate that one atom of silver is differently linked from the others, which give silver chloride. It may be that the compound is a solid solution of silver and the compound Ag_3AsCl_3 , which would be the analogue of the bromine compound.

When copper is used instead of silver, the *compounds* $7\text{Cu}_2\text{AsCl}_3$ and $7\text{Cu}_2\text{AsBr}_3$ are obtained. They behave very similarly to the silver compounds, except that ammonium hydroxide, potassium hydroxide, and hydrochloric acid transform the copper into cuprous oxide or chloride; magnesium phenyl bromide gives triphenylarsine.

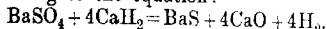
Substances of similar properties are obtained by the action of arsenic vapour at 500° on silver chloride or bromide and on cuprous chloride; it follows that the decomposition of these compounds at high temperatures, whereby arsenic is produced, is reversible.

T. S. P.

Calcium Hydride. WILHELM MOLDENHAUER and C. ROLL-HANSEN (*Zeitsch. anorg. Chem.*, 1913, 82, 130—140).—Experiments to determine the dissociation pressure of calcium hydride, using a nickel boat in a porcelain tube, gave a marked dissociation from 600° , reaching one atmosphere below 800° . On the other hand, calcium hydride is readily prepared by heating calcium in hydrogen at 830° , so that the pressures measured above cannot be true dissociation pressures. The porcelain tube is attacked. If lined with iron, quite different results are obtained, the pressure being only 11 mm. at 780° and 705 mm. at 1027° . A second hydride, CaH_2 , also exists, having its own dissociation pressure, and this compound appears to be volatile.

The heat of formation of CaH_2 is calculated to be about 21,000 cal., and of CaH from CaH_2 and hydrogen also about 21,000 cal., making 42,000 cal. for the heat of formation of calcium hydride from liquid calcium and hydrogen, whilst Guntz and Bassett (*A.*, 1905, ii, 300) found 46,200 cal. from solid calcium. C. H. D.

The Action of Calcium Hydride on Sulphates. ERICH EBELER and K. HEERDEGEN (*Ber.*, 1913, 46, 2264—2267).—When a mixture of barium sulphate and calcium hydride is ignited by a fuse similar to that used in the thermit reaction, vigorous action takes place according to the equation:



The hydrogen apparently does not take part in the reduction, since water is not formed; of course, the reaction product may consist partly of barium oxide and calcium sulphide.

If the product of reaction is added to water in small portions at a time in order to decompose excess of calcium hydride, and then warmed with hydrochloric acid, complete solution is readily obtained; the barium may be quantitatively precipitated from solution by saturation with hydrogen chloride (compare Ebler, *A.*, 1909, ii, 347).

The above reaction forms a ready method of getting insoluble sulphates into solution, a large number of sulphates reacting. Sulphates of the heavy metals sometimes give the metal itself; the reaction with lead sulphate proceeds with explosive violence.

Further experiments are being made with the sulphates of thorium and cerium and other rare earth metals. T. S. P.

Melting Points of Some Refractory Oxides. CLARENCE W. KANOLT (*J. Washington Acad. Sci.*, 1913, 3, 315—318).—An Arsen graphite resistance furnace is used, the temperatures being determined by means of a Holborn-Kurlbaum optical pyrometer, sighted vertically downward through a glass window. Lime and

magnesia volatilise completely in a vacuum without melting, and in such cases an atmosphere of hydrogen is used.

Magnesia is melted in graphite crucibles, but lime forms carbide, and must be melted in a tungsten crucible, or by making a tube of lime, through which hydrogen is passed and down which the pyrometer is sighted. Alumina and chromium oxide are melted in tungsten crucibles in a vacuum.

The following results are obtained: MgO, 2800°; CaO, 2570°; Al₂O₃, 2050°; Cr₂O₃, 1990°.

C. H. D.

Peroxide, Ozone, and Nitrous Acid in Calcium Hydroxide and Aragonite. WILHELM VAUBEL (*J. pr. Chem.*, 1913, [ii], 88, 61–72. Compare A., 1912, ii, 1180).—According to Ditz (this vol., ii, 320), the starch-iodide reaction shown by calcium hydroxide and aragonite is due to the presence of small quantities of nitrites and of ferric compounds, and not to the presence of calcium peroxide, since neither aragonite nor calcium hydroxide give the usual peroxide reactions with titanin and vanadic acids.

The author points out, however, that the negative results obtained in the latter reactions furnish no criterion as to the absence of a peroxide, for calcium peroxide itself in the presence of an excess of calcium hydroxide does not react with either vanadic or titanin acids.

That the starch-iodide reaction is not due to the presence of nitrite is conclusively proved by the fact that a calcium hydroxide, which gave a distinct reaction with starch-potassium iodide, did not show the usual nitrite reactions with sulphanilic acid and phenol, resorcinol, pyrogallol, guaiacol, or brucine, although positive reactions were obtained at once on the addition of a trace of nitrite to the calcium hydroxide.

Further, it is improbable that the blue coloration is due to ferric compounds, for the latter react only slowly with starch-potassium iodide, whilst in many cases the blue coloration with calcium hydroxide develops instantly. Moreover, the estimation of the peroxide by titration of the liberated iodine with sodium thio-sulphate is in good agreement with the results obtained by direct titration with permanganate, which would not be the case if the starch-iodide reaction were due to the presence of ferric compounds. Finally, although the peroxide in aragonite and calcium hydroxide cannot be detected by the uranyl nitrate, vanadic, titanin, and chromic acid reactions on account of the disturbing influence of the excess of calcium hydroxide, positive results have been obtained with the benzidine and *m*-phenylenediamine reactions.

The paper contains a summary in tabular form of thirty-eight reactions which may be used for the detection of ozone, nitrous acid, and hydrogen peroxide.

F. B.

Reduction of Tricalcium Phosphate by Hydrogen. ARNOLD LAUSTEUR (*Eighth. Inter. Cong. App. Chem.*, 1912, 2, 171–174).—At 1300° calcium phosphate is reduced by hydrogen to a mixture of

calcium oxide and phosphorus. Only traces of phosphorus hydride and calcium phosphide are produced during the reaction. It is probable that a basic phosphate is produced as an intermediate product.

Carbon monoxide has no reducing properties towards calcium phosphate at 1300°.

T. S. P.

Theory of Luminescent Stones and their Various Coloured Phosphorescence. LUDWIG VANINO (*J. pr. Chem.*, 1913, [ii], 88, 77—79. Compare this vol., ii, 591).—According to the author, luminescent sulphide stones on exposure to light become superficially transformed into modifications of higher energy content. The transformation is reversible, the phosphorescence after exposure to light representing the transformation into the original modification of lower energy content.

With respect to the effect of traces of impurities in modifying the colour of the phosphorescent light, the author considers that their action is not a chemical one, but is similar to that of the sensitisers in photochemical processes; the energy which becomes available during the transformation of the sulphides is converted by them into light energy.

The different phosphorescent colours exhibited by different parts of one and the same stone, is found to be due to a difference in the temperature to which the stones were exposed during their preparation; thus, a mixed calcium-strontium stone containing traces of rubidium showed, in its upper part, a light blue phosphorescence, whilst the lower part, which had been more strongly heated, exhibited a deep violet phosphorescence.

F. B.

Glucinum Peroxide. A. S. KOMAROVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 608—613).—Attempts to prepare glucinum peroxide by the action of hydrogen peroxide on hydrated glucinum oxide resulted only in the formation of the compound $3\text{GfO}_2 \cdot 4\text{H}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$, containing hydrogen peroxide of crystallisation.

With basic glucinum carbonate of the composition $\text{GfCO}_3 \cdot 5\text{GfO} + 8\text{H}_2\text{O}$ hydrogen peroxide yields the *basic peroxide*, $2\text{GfO}_3 \cdot 3\text{GfO} + 8\frac{1}{2}\text{H}_2\text{O}$, which is moderately stable, and exhibits all the usual properties of peroxides.

T. H. P.

Glucinum Sulphide. K. MIELEITNER and HERMANN STEINMETZ (*Zeitsch. anorg. Chem.*, 1913, 82, 92—96).—Glucinum sulphide may be prepared by heating glucinum chloride in hydrogen sulphide, previously purified by means of a chromous salt and phosphoric oxide. For analysis the product is heated in a sealed tube with nitric acid and silver nitrate. The silver chloride is collected, silver is removed from the filtrate by hydrochloric acid, and the sulphur is estimated as barium sulphate. Glucinum is estimated in the filtrate. The product contains 97—98% of sulphide.

Glucinum sulphide is a white, amorphous mass. It is little decomposed by water, even when boiling, but readily by acids, including atmospheric carbon dioxide. It burns with a bright

flame and separation of sulphur in contact with concentrated nitric acid. Dry hydrogen chloride at a red heat converts it into the chloride, and bromine vapour into the bromide. A poly-sulphide has not been obtained. C. H. D.

The Nature of Alkaline Glucinum Solutions. BENNO BLEYER and S. W. KAUFMANN (*Zeitsch. anorg. Chem.*, 1913, 82, 71—91).—When a solution of glucinum sulphate is dropped into potassium hydroxide, a saturation point is reached, depending on the concentration of the hydroxide. From the solution saturated with the hydroxide *A* a second hydroxide, *B*, is obtained, and on collecting and drying *B* a third modification, *C*, which is still less soluble, is obtained. The solubility of the three modifications has been determined. When the relative concentrations of glucinum and potassium hydroxide are plotted against one another, *A* and *B* yield straight lines, whilst *C*, like the corresponding modification of zinc hydroxide, shows a marked curvature (compare Wood, T., 1910, 97, 878). Analysis of the hydroxides, after washing with absolute alcohol, gives the compositions *A*, $\text{H}_2\text{Glu}_2\text{O}_3$; *B* and *C*, H_2GluO_2 . The ionic products for *A*, *B*, and *C* respectively are K_1 , 0.73×10^{-29} ; K_2 , 0.28×10^{-29} ; K_3 , 0.144×10^{-29} , and the constants of acid dissociation are 1.5×10^{-12} , 0.56×10^{-12} , and 0.29×10^{-12} . These are minimum values. Fresh glucinum hydroxide is a somewhat stronger acid than zinc hydroxide in the corresponding condition. C. H. D.

Thermal Dissociation of Magnesium Carbonate. ROBERT MARC and A. ŠIMEK (*Zeitsch. anorg. Chem.*, 1913, 82, 17—49). Compare Grünberg, this vol., ii, 516).—According to Brill (A., 1905, ii, 522), the dissociation of magnesium carbonate by heat takes place in stages, seven basic carbonates being formed. Discontinuities were not observed by Friedrich and Smith (this vol., ii, 28). It is now shown that the dissociation proceeds very slowly in the dry substance, but is accelerated by the presence of moisture, this factor accounting for the divergent results.

Precipitated magnesium carbonate always contains water. Anhydrous rhombohedral artificial magnesite is obtained by heating 10 grams of precipitated carbonate with 300 c.c. of water and a few grams of solid carbon dioxide at 185° in an autoclave under 20 to 30 atmospheres pressure. Even this preparation retains water very obstinately. The dissociation at 350° is accelerated by mixing the carbonate with fused potassium nitrate. Manometric measurements with the dried carbonate give inconclusive results owing to the slowness with which equilibrium is reached.

Kinetic experiments have been made by heating the material in a platinum boat in a stream of dry or moist air. The latter accelerates the decomposition. The velocity of dissociation gradually diminishes with time.

The dissociation in presence of water-vapour has been determined. This is permissible, as the dissociation pressure of magnesium hydroxide is equal to one atmosphere at 180° , so that the hydroxide is

not formed during the experiments with carbonate. Heating in sealed tubes, and analysing the gaseous contents after removal from the furnace, does not yield satisfactory results, as re-combination takes place with appreciable velocity. This is avoided by mixing with potassium nitrate. A mixture of 1 part of magnesium carbonate and 3 parts of potassium nitrate allows of an accurate measurement of the dissociation. The pressure of one atmosphere is reached at 402°. The heat of dissociation is calculated to be -23,200 cal.

C. H. D.

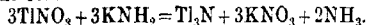
The Influence of Foreign Metals on the Rolling of Zinc. EUGÈNE PROST and A. VAN DE CASTEELE (*Bull. Soc. chim. Belg.*, 1913, 27, 175-189).—The question of the influence of the presence of foreign metals on the rolling of zinc is little understood. The authors have taken for their experiments refined zinc (containing about 1% lead and a few hundredths % of cadmium and iron), and have added in various cases cadmium, tin, antimony, copper, arsenic, and iron. The results indicate that under the usual practical conditions of rolling the content of lead should not exceed 1.25%, and that of cadmium 0.2%; these limits are well above the quantities generally present in practice. The quantity of iron, arsenic, antimony, and tin (of which the last is most harmful) should be kept as low as possible, especially in view of the fact that the effect of these metals when present together is an additive one.

D. F. T.

A Process for Rendering Innocuous a Water Supply Contaminated with Lead. PAUL SCHMIDT (*Arch. Hygiene*, 1913, 80, 70-73).—The colloiddally dissolved lead hydroxide can be separated by filtration through a Berkfeld filter.

S. B. S.

The Action of Potassium Amide on Thallium Nitrate in Liquid Ammonia Solutions. EDWARD C. FRANKLIN (*Eighth. Inter. Cong. App. Chem.*, 1912, 2, 103).—When a solution of potassium amide in liquid ammonia is added to a similar solution of thallium nitrate, a black precipitate of thallous nitride is formed in accordance with the reaction:



Thallium nitride dissolves readily in solutions of potassium amide in liquid ammonia. When the ammonio-base is used in limited quantity a yellow solution is formed, from which *potassium ammonothallite*, $\text{TlNK}_2\cdot 4\text{NH}_3$, may be obtained as beautiful, yellow crystals. This compound loses successive portions of its ammonia of crystallisation to form products represented by the respective formulæ: $\text{TlNK}_2\cdot 2\text{NH}_3$ and $\text{TlNK}_2\cdot \text{NH}_3$.

When thallium nitride is dissolved in excess of potassium amide, solutions are formed which give well-crystallised products, which are considered to be isomorphous mixtures either of potassium ammonothallite with potassium amide or of potassium amide and the unknown thallium anide.

T. S. P.

Variation of Resilience in Copper and Some of its Alloys with Temperature. LÉON GUILLET and VICTOR BERNARD (*Compt. rend.*, 1913, 156, 1899—1901).—The methods of examination used are those already published by Guillet and Révillon (*Rev. Metall.*, 1909, 6, 94). The range of temperatures was from 0° to 1100°. Analyses of all the materials tested are quoted. With the exception of copper-nickel alloy (Cu, 77.9; Ni, 20.2; Zn, 1.7; Fe, 0.1%), all the alloys tested showed maximum fragility beginning at 300—400°, and disappearing at about 700°. In many cases the greatest resilience was exhibited at 100°.

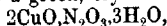
Brass (Cu, 90.6; Zn, 9.3%) becomes less fragile between 700° and 900°, whilst the addition of lead (Cu, 90.3; Zn, 8.2; Pb, 1.3%) leads to the alloy showing maximum fragility up to 900°. Brasses containing 80.9 and 70% of copper respectively were fragile at 700° to 850°, whilst those with 61.8 and 61.3% of copper began to improve at 700°. Copper-nickel alloy begins to be fragile at 600°, but improves at 1000°. German silver (Cu, 54.1; Zn, 25.4; Ni, 19.7; Fe, 0.4%) begins to be fragile at 300°, and is less resilient all through than copper-nickel alloy. Aluminium-bronze (Cu, 90.0; Al, 9.8; Fe, 0.2%) showed discontinuity between 600° and 800°, and determinations could not be made between these temperatures. Addition of iron (Cu, 88.5; Al, 7.5; Fe, 3.7) caused fragility to lessen at 700°. The results of the investigation are shown graphically in the original.

T. A. H.

Complex Copper Nitrites. ALBIN KURTENACKER (*Zeitsch. anorg. Chem.*, 1913, 82, 204—215).—Potassium copper nitrite, $K_3Cu(NO_2)_5$, is obtained by mixing cold saturated solutions of copper sulphate and potassium nitrite, adding methyl alcohol, filtering, and adding ethyl acetate to the clear, green filtrate. Long crystals of the salt separate. The salt is stable when pure.

Rubidium copper nitrite, $Rb_3Cu(NO_2)_5$, closely resembles the potassium salt.

Barium copper nitrite, $Ba[Cu(NO_2)_2]_2$, from copper and barium nitrites, forms green double pyramids. Other compounds have not been obtained. Evaporating copper nitrite with zinc, nickel, or manganese nitrite yields a green, crystalline compound,



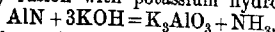
which contains traces of the added metal. The presence of a complex anion in copper nitrite solution is shown qualitatively, but even concentrated solutions contain an excess of the normal ions. Two basic copper nitrites are also described: $3Cu(OH)_2.Cu(NO_2)_2$ and $2Cu(OH)_2.Cu(NO_2)_2$.

C. H. D.

Thermal Analysis of Clays. RUBY WALLACH (*Compt. rend.*, 1913, 157, 48—50).—A comparative thermal study of kaolin, a pure clay, white mica, and some clays of known origin. The samples were heated in an electric furnace, and the temperatures of the furnace and substance noted. Curves are given showing the relationship between the furnace temperature and the temperature difference between furnace and substance. The results indicate no definite means of analysis.

W. G.

The Reactions of Aluminium Nitride. FRITZ FICHTER and ADOLF SPENGLER (*Zeitsch. anorg. Chem.*, 1913, 82, 192—203. Compare A., 1907, ii, 691).—Aluminium nitride is best prepared by passing nitrogen over aluminium powder at 800°. A reaction sets in, and the temperature rises to 1300°. Impurities are removed by treatment with dry hydrogen chloride at a red heat. The nitride may be decomposed by fusion with potassium hydroxide,



or by heating with a mixture of 10 c.c. of concentrated sulphuric acid with 40 c.c. of water. Dry halogens act slowly on the nitride; chlorine decomposes it at 760°: $2\text{AlN} + 3\text{Cl}_2 = 2\text{AlCl}_3 + \text{N}_2$. Sulphur chloride vapours act more rapidly. Hydrogen is without action.

Lead dichromate decomposes it completely, but the reaction with sodium peroxide remains incomplete, and nitrate is also formed. Sulphur, phosphorus, and carbon disulphide partly displace nitrogen, but phosphorus trichloride is without action. Carbon is without action at 1200°, and carbon dioxide merely oxidises, but a mixture of sodium and potassium carbonates with carbon converts a large part of the nitride into cyanide. Alcohol forms triethylamine at 230°.

C. H. D.

The So-Called Manganese Trioxide. FREDERICK R. LANKSHEAR (*Zeitsch. anorg. Chem.*, 1913, 82, 97—102. Compare P., 1912, 198).—A 6% solution of potassium permanganate is allowed to drop into a cooled mixture of one part of sodium hydrogen carbonate to four parts of anhydrous sodium carbonate. The gas is condensed in a flask cooled with liquid air. After evaporating the carbon dioxide, a dark red, amorphous solid, m. p. -6° , remains. The ratio of permanganate to manganese dioxide is about 4.8:1. The conclusion is confirmed that the gas is an impure hydrated permanganic acid.

C. H. D.

The Critical Ranges, A_1 and A_2 , of Pure Iron. GEORGE K. BURGESS and J. J. CROWE (*J. Washington Acad. Sci.*, 1913, 3, 329—332).—Five separate preparations of electrolytic iron have been used, in quantities of from 21 to 31 grams. Both the inverse rate and differential methods have been employed. Ac_2 is as pronounced as Ar_2 for all the samples, and for metal re-melted in a vacuum the position of Ac_2 and Ar_2 is identical. A_2 and A_3 appear to be different in kind.

C. H. D.

Formation of Rust under Protecting [Paint] Layers. ERICH PFLEIDERER (*Zeitsch. Elektrochem.*, 1913, 19, 507—510).—Polemical. The author shows that the theory of Liebreich and Spitzer (A., 1912, ii, 259) with regard to the rusting of painted iron is unnecessary, and that their measurements will not bear the interpretation placed on them.

J. F. S.

Formation of Rust under Protecting [Paint] Layers. ERICH LIEBREICH and FRITZ SPITZER (*Zeitsch. Elektrochem.*, 1913, 19, 510—513).—Polemical; an answer to Pfeiderer (preceding abstract).

J. F. S.

The Absorption of Iron Pentacarbonyl by Iron. A. STOFFEL (*Eighth. Inter. Cong. App. Chem.*, 1912, 2, 225—233).—The first part of the paper is a re-statement of results already published (A., 1912, ii, 986).

The author has devised a method by which he is able to estimate both the gaseous and adsorbed iron pentacarbonyl. The curves showing the relation between the concentration in the vapour and solid phases are exactly of the form of adsorption isotherms, from which the conclusion is drawn that the iron pentacarbonyl is adsorbed by the iron. This adsorption explains the slowness of the reaction between iron and carbon monoxide. T. S. P.

Neutralisation of Chromic Acid. RENÉ DUBRISAY (*Compt. rend.*, 1913, 156, 1902—1904).—The method already described (this vol., ii, 388) has been applied to the investigation of the neutralisation of chromic acid by sodium hydroxide and by ammonia. The results show that chromic acid differs from a strong dibasic acid, such as sulphuric acid, in exhibiting a constant surface tension only until the first acid function is neutralised, after which the surface tension decreases gradually but slightly until the second is neutralised, when, as usual, a great decrease occurs. These results are in harmony with those recorded by Berthelot (A., 1883, 642, 707), Sabatier (A., 1886, 692), and Gröger (A., 1908, ii, 690) as a result of other methods of investigation. T. A. H.

Hydrates of Uronic Anhydride and Heat of Formation of Uranyl Nitrate. ROBERT DE FORCRAND (*Compt. rend.*, 1913, 156, 1954—1958).—The uranic anhydride, UO_3 , used by the author was prepared by heating uranyl nitrate at 290—300° for a considerable time, taking care to avoid fusion. If the heating takes place at 550—600° fusion occurs, and a polymeride of unknown molecular weight results. The dihydrate, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, was obtained from the anhydride by the ordinary methods, and the monohydrate, $\text{UO}_3 \cdot \text{H}_2\text{O}$, by heating the dihydrate at 80° in dry air.

As the basis of his measurements the author assumes that the heat of formation of uranic anhydride from the oxide UO_2 and oxygen is the same, and has the heat of formation of the oxide U_3O_8 from UO_2 and oxygen, namely, 37·65 Cal. (compare Mixer, A., 1912, ii, 899). The following thermochemical values were obtained: Heats of solution in dilute nitric acid of: UO_3 , 19·803 Cal.; $\text{UO}_3 \cdot \text{H}_2\text{O}$, 14·846 Cal.; $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, 12·375 Cal.; $\text{UO}_3 + 3\text{O}_2 + \text{N}_2 = \text{UO}_2(\text{NO}_3)_2(\text{solid}) + 67·25$ Cal., or $\text{UO}_2(\text{NO}_3)_2(\text{aq}) + 86·25$ Cal.; $\text{UO}_2(\text{NO}_3)_2 = \text{N}_2\text{O}_5(\text{gas}) + \text{UO}_3 - 30·60$ Cal.; $\text{UO}_3 + \text{H}_2\text{O}(\text{gas}) = \text{H}_2\text{UO}_4 + 14·62$ Cal.; $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} = \text{UO}_2(\text{NO}_3)_2 + 2\text{H}_2\text{O}(\text{gas}) - 33·27$ Cal.; $\text{H}_2\text{UO}_4 + \text{UO}_2(\text{NO}_3)_2 = \text{basic nitrate} + 4·03$ Cal.

T. S. P.

The Preparation of Thoria from Monazite Sand by means of Hypophosphoric Acid. Detection of Cerium with an Alkaline Solution of Ammonium Tartrate. FRITZ WIRTH (*Chem. Zeit.*, 1913, 37, 773—774).—In the precipitation of thoria as

hypophosphate (compare A., 1912, ii, 948) difficulties may arise from the formation of sparingly soluble double sulphates of sodium and the cerium earths when sodium hypophosphate is added to the sulphuric acid solution of the monazite sand. These difficulties may be avoided if the anion of hypophosphoric acid is formed *in situ* in the acid solution. This may be accomplished either by direct oxidation of phosphorus in the solution, or by the anodic oxidation of copper phosphide, using the acid solution as electrolyte.

Thorium can be completely precipitated as hypophosphate by the addition of much sodium hypophosphate to a boiling, slightly ammoniacal solution of thorium tartrate if care is taken to keep the solution ammoniacal.

The formation of an intense, yellowish-brown colour on the oxidation of ammoniacal solutions of cerium tartrate is a very sensitive test for cerium. The oxidation takes place on exposing the solution to the air; if less than 0.1—0.5% of cerium is present it is necessary to boil the solution. If hydrogen peroxide is used as the oxidising agent, the test is sensitive to 0.0002 gm. of CeO_2 per 100 c.c.

T. S. P.

Action of Boiling Sulphuric Acid on Platinum. LE ROY W. McCAY (*English Inter. Cong. App. Chem.*, 1912, 1, 351—359).—Boiling sulphuric acid dissolves platinum in considerable amounts (in one experiment when boiling 10 c.c. of acid in a covered dish for one hour, 0.0038 gram of Pt was dissolved). The attack is not due to atmospheric oxygen, for the same thing happens when heating in a current of an inert gas. Excess of sulphur dioxide which may be conveniently generated by introducing a piece of sulphur into the hot acid, or else be passed in the form of a current, prevents almost entirely the solvent action.

If it is assumed that at the temperature of attack there is a slight dissociation of the acid, thus liberating oxygen which would cause the action; this would account for the protective power of such reducing substances as excess of sulphur dioxide, arsenious and antimonious oxides.

L. DE K.

Alkali Osmibromides (Hexabromo-osmeates). ALEXANDER GUTBIER (*Ber.*, 1913, 46, 2098—2103).—The observation of Moraht and Wischin (A., 1893, ii, 380) that finely-divided osmium does not enter into reaction with bromine was confirmed. It was found that the osmibromides could not be obtained from the osmichlorides in all cases by treatment with hydrobromic acid, owing to similar reactions occurring to those which take place with the corresponding iridium compounds (compare Gutbier and Riess, A., 1909, ii, 1025); only the ammonium and potassium osmibromides could be obtained in this way.

The most satisfactory method for obtaining sodium osmibromide was by the decomposition of sodium sulphito-osmate (schweflig-osmiumsaure Natrium), $3\text{Na}_2\text{O} \cdot \text{OsO}_3 \cdot 4\text{SO}_2 \cdot 5\text{H}_2\text{O}$ (Rosenheim and Sasserath, A., 1899, ii, 664), with boiling concentrated hydrobromic acid, D 1.45. The other alkali salts were readily obtained from the

sodium salt by precipitation with the corresponding alkali bromides from not too concentrated solution. The sodium, ammonium, and potassium salts have already been described by Rosenheim and Sasserath (*loc. cit.*).

Rubidium osmibromide, Rb_2OsBr_6 , forms a reddish-brown, fine-crystalline powder. *Caesium osmibromide*, Cs_2OsBr_6 , is a dark reddish-brown, microcrystalline powder. T. S. P.

Mineralogical Chemistry.

Platinum Sands from New Zealand. R. A. FARQUHARSON (*Zeitsch. Kryst. Min.*, 1913, 52, 419; from *Trans. New Zealand Inst.*, 1910, 43, 448—482).—Platinum is found in several of the gold-fields of New Zealand. Near Orepuki, in Otago, it occurs in sands and shore deposits in the form of rounded scales; analysis gave:

Pt.	Ir.	Pd.	Rh.	An.	Fe.	Cu.	Iridosmine.	Os.	Total.
74.61	1.30	1.36	3.52	0.39	5.08	0.15	14.32	trace	100.73

The gabbro of the neighbourhood contains no platinum, and the metal was probably derived from serpentine of the interior.

L. J. S.

Platiniferous Dunites. SANTIAGO PIÑA DE RUBIES and F. COMA y ROCA (*Anal. Fis. Quim.*, 1913, 11, 334—339).—Two specimens of dunite from Diudinsky had the compositions of olivines with 1.16% and 1.41% respectively of chromite.

G. D. L.

Helium in Glucinum Minerals. II. ARNALDO PIUTTI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 671—672. Compare this vol., ii, 419).—The author has examined six further specimens of phenacite from different localities, and has been unable to detect helium in them. The minerals show no radioactivity.

R. V. S.

Calcite Crystals from a Water-Tank. RUSSELL F. GWINNELL (*Min. Mag.*, 1913, 16, 345—347).—The material consists of a glistening, white, crystalline powder, and it was deposited in a tank into which water was led from a spring rising from the ferruginous marlstone at Belton Park, near Grantham, Lincolnshire. It consists entirely of minute crystals having the form of the primary rhombohedron, $r(10\bar{1}1)$, of calcite. D 2.71. Analysis, by M. B. CHAPMAN, gave:

CaCO_3	Al_2O_3	Fe_2O_3	SiO_2	Insol.	Total.
95.65	0.93	0.21	3.14	0.6	99.99

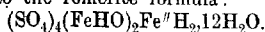
L. J. S.

Triplite from Eastern Nevada. FRANK L. HESS and W. F. HUNT (*Amer. J. Sci.*, 1913, [iv], 36, 51—54).—Small, irregular masses of triplite occur with wolframite, bismuth minerals, etc., in quartz veins in the Reagan mining district, White Pine County. The material is light salmon-pink in colour with a vitreous lustre, and has cleavages in two directions. D 3.79, H 4—4½; refractive indices α 1.650, β 1.660, γ 1.672. Analysis gave the following results, agreeing with the formula $3\text{MnO} \cdot \text{P}_2\text{O}_5 \cdot \text{MnF}_2$:

MnO.	FeO.	CaO.	MgO.	P ₂ O ₅ .	F.	Total.
57.63	1.68	2.86	1.21	31.84	7.77	102.99

The mineral thus lies at the manganese end of the series, and it differs from those richer in iron in its colour. L. J. S.

Constitution and Genesis of Ferric Sulphates. VIII. Botryogen and Römerite; Copiapite. RUDOLF SCHARIZER (*Zeitsch. Kryst. Min.*, 1913, 52, 372—398).—The formula of botryogen written in the form $(\text{SO}_4)_4(\text{FeHO})_2(\text{MgHO})_2\text{H}_2 \cdot 12\text{H}_2\text{O}$ shows a relation to the römerite formula:



Although botryogen is monoclinic and römerite is triclinic, the axial ratios can be so converted as to show a close relationship. The available crystallographic data of copiapite are also discussed, and a relation brought out between these and the data for botryogen. Copiapites fall chemically into two groups, namely, those without and those with bivalent oxides ($\text{RO} = \text{MgO}$, FeO , ZnO , MnO). Analyses of material belonging to the first group are: I, native copiapite from Sierra de l'Alcapa rossa, II, artificial copiapite, and of the second group: III—IV, copiapite from South America; and V—VI, from Rammelsberg, Harz:

	SO ₃ .	Fe ₂ O ₃ .	FeO.	ZnO.	MgO.	H ₂ O.	Insol.	Total.
I.	38.62	30.24	—	—	—	30.75	0.90	100.51
II.	38.72	30.68	—	—	—	30.60	—	100.00
III.	38.44	26.36	1.53	2.11	0.98	30.09	0.15	99.66
IV.	38.47	26.78	1.51	1.67	0.66	30.07	0.27	99.43
V.	38.27	26.39	0.33	1.45	1.73	30.60	0.79	99.56
VI.	38.22	26.19	0.45	2.47	0.85	31.33	0.40	99.91

For the first group the formula is $(\text{HOFe})_4(\text{HSO}_4)_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$, and in the second group there is in addition the radicle $(\text{RSO}_4)_x \cdot x\text{H}_2\text{O}$. L. J. S.

Chemical Composition of Dysanalyte from Vogtsburg in Kaiserstuhl. WILHELM MEIGEN and E. HUGEL (*Zeitsch. anorg. Chem.*, 1913, 82, 242—248. Compare Hauser, A., 1909, ii, 60).—Hauser's method of analysis gives low values for columbium. The powdered material is purified by treatment with hot dilute hydrochloric acid and potassium hydroxide, which are without action on dysanalyte. The mineral has D 4.26 and H 5.5. It is fused with potassium hydrogen sulphate, extracted with water containing sulphuric acid and hydrogen peroxide, and filtered. The residue, after ignition with hydrofluoric acid, is again fused with potassium hydrogen sulphate. The filtrates, after removal of hydrogen per-

oxide, are twice precipitated with ammonium carbonate. The precipitate is dissolved in sulphuric acid, neutralised carefully with ammonia, and mixed with sulphurous acid in large excess. Titanic and columbic acids are precipitated quantitatively on warming. The precipitate is dissolved in sulphuric acid and hydrogen peroxide, and again precipitated. Titanium and columbium are separated by Weiss and Landecker's method (A., 1909, ii, 942). Two specimens gave the following analyses (mean of several determinations):

	SiO ₂	TiO ₂	Ch ₂ O ₃	CaO	Ce ₂ O ₃ (La ₂ O ₃)	FeO	Al ₂ O ₃	K ₂ O	Na ₂ O	MnO	MgO	Total
I.	0.29	48.31	16.12	21.63	3.32	5.35	1.25	0.39	4.20	0.02	—	100.88
II.	0.33	38.70	25.99	23.51	3.08	5.69	0.82	0.44	1.72	—	—	100.28

C. H. D.

Zirkelite from Ceylon. GEORGE S. BLAKE (*Min. Mag.*, 1913, 16, 309—316).—The materials analysed were found as grains and small pebbles in the gem-gravels at various localities in the Sabaragamuwa province. They are brownish-black with sub-metallic lustre and sub-conchoidal fracture, and range in density from 4.72 to 5.22; hardness, 5½—6. Three varieties are distinguished according to the relative amounts of thorium and uranium oxides present; these are represented respectively by analyses I–III, IV and V, and VI. The material is slowly decomposed by hydrochloric acid, but readily by hydrofluoric. A 20-gram sample, heated with hydrogen potassium sulphate, yielded 134.9 c.c. of gas containing: CO₂, 40.2; H, 10.2; N, 34.9; He, 14.7%:

	ThO ₂	U ₂ O ₅	ZrO ₂	TiO ₂	(Ca, La, Di)O ₃	Y ₂ O ₃	FeO	CaO	MgO	PbO	H ₂ O	Total	Sp. gr.
I.	20.17	—	—	—	3.61*	0.96	—	—	—	—	—	—	5.2
II.†	20.44	1.06	30.73	29.50	2.68	1.08	4.07	6.87	2.34	0.38	0.46	89.64	5.0–5.1
III.	18.78	0.65	32.56	30.95	1.40	0.40	4.42	6.78	3.04	—	1.05	100.03	4.72
IV.	8.33	4.66	34.19	36.26	—	0.32	4.72	8.55	1.33	—	1.70	100.06	4.47
V.‡	8.51	2.08	32.64	36.06	—	0.83	4.65	9.35	1.08	—	1.74	99.20	4.32
VI.	0.23	14.31	35.27	34.87	—	—	3.78	8.18	1.96	0.44	1.68	100.67	4.40

* Ce₂O₃, 1.44; (La, Di)₂O₃, 2.17. † Also MnO, 0.03. ‡ Also Al₂O₃, 2.26.

Material from the same samples as anal. IV–VI was examined crystallographically by G. F. H. SMITH. The rough crystals are hexagonal ($a:c=1:1.1647$) and twinned. It is suggested that the original zirkelite (A., 1895, ii, 508) may be rhombohedral or hexagonal rather than cubic.

L. J. S.

Talc from Hozsuret, Hungary. H. MICHEL (*Tech. Min. Petr. Mitt.*, 1912 [i.e. 1913], 31, 331).—The following analysis is of a very pure sample of talc, which in thick pieces shows a blue or green colour. The material is optically negative, with $2V=7^\circ$, $\alpha=1.538$, $\gamma=1.588$:

SiO ₂	Al ₂ O ₃	FeO	Cr ₂ O ₃	CaO	MgO	H ₂ O	Hygros. H ₂ O	Total
61.75	3.52	1.13	trace	trace	28.28	5.05	0.23	99.96

L. J. S.

Solid Solution in Minerals: The Constant Composition of Albite. HARRY W. FOOTE and WALTER M. BRADLEY (*Amer. J. Sci.*, 1913, [iv], 36, 47—50).—The variable compositions of nephelite, analcite, and pyrrhotite have recently been explained by the presence of other substances (not isomorphous) in solid solution (A., 1911, ii, 122; 1912, ii, 568, 354). It is found that nephelite contains more silica when it is intimately associated with albite; and if solid solutions of this kind were common amongst minerals it would be expected that their composition might vary according to their associations. In order to test this view, analyses are given of albite associated with quartz from Amelia Court House, Virginia (anal. I by Robertson in 1884; II by Musgrave, 1882), and of albite associated with corundum and nephelite in corundum-syenite from Brudenell, Renfrew Co., Ontario:

	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	H ₂ O	Total
I.	67.06	21.72	1.59	0.03	10.01	0.39	—	100.80
II.	68.44	19.35	—	—	11.67	0.43	—	99.89
III.	63.86	23.32	3.76	—	9.20	0.16	0.24	100.54

Deducting anorthite, the ratios of SiO₂:Al₂O₃:(Na₂O+K₂O) are respectively 6.00:1.04:0.93, 6.00:1.00:1.02, and 6.00:1.04:0.94.

These slight variations may be explained by errors of analysis or the presence of impurities; and they do not support the view of any solid solution of quartz, nephelite, or corundum in albite.

L. J. S.

Nefedieffite from the Neighbourhood of Troickosavsk [Siberia]. ALEX. FERSMAN and L. CITLIADZEV (*Bull. Acad. Sci. St. Petersbourg*, 1913, 677—687).—The authors describe a pale rose-coloured mineral found near Troickosavsk, and sold in large quantities in Irkutsk under the name of talc. It occurs in compact masses having a splintery fracture, and is fatty to the feel. Its hardness is about 1.5, and it cuts like hard soap. The intensity of its colour varies somewhat in different samples, and apparently depends on the presence of traces of manganese. Its composition is:

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	H ₂ O (below 100°)	H ₂ O (above 100°)	Loss on ignition	Total
51.33	17.75	0.62	2.83	4.61	9.51	13.66	23.17	100.31

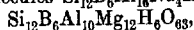
These results are in close agreement with those obtained for nefedieffite, the formula of the latter being probably:

$1(\text{MgO}, \text{CaO}, \text{FeO}, \text{K}_2\text{O}, \text{Na}_2\text{O}) \cdot 1(\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3) \cdot 5\text{SiO}_2 \cdot 4\text{H}_2\text{O} + 3\text{H}_2\text{O}$, or $4\text{R}_2\text{R}'/\text{Si}_5\text{O}_{11} \cdot 7\text{H}_2\text{O}$. It sometimes undergoes conversion into montmorillonite, from which it differs in fusibility and in its resistance to the action of acids.

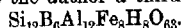
Nefedieffite probably forms the chief constituent of Fuller's earth, and allied to it are the majority of the natural soaps, including keffekilite, confolensite, soapstone, saponite, pseudosteatite, etc., as well as the so-called "Basaltsteinmark."

T. H. P.

Tourmaline Group. PAUL REINER (*Verh. naturhist.-med. Ver. Heidelberg*, 1913, 12, 262—317; and *Diss. Heidelberg*, 1913, 1—57).—A detailed discussion of the formulæ proposed by Penfield and Foote (A., 1899, ii, 304), Tschermak (A., 1900, ii, 217), and Wülfing (A., 1901, ii, 65). Wülfing assumed the isomorphous mixing of the two molecules $\text{Si}_{12}\text{B}_6\text{Al}_{12}\text{Na}_4\text{H}_5\text{O}_{83}$ and



and he now suggests to the author a third molecule,



Re-calculations of many previously-published analyses are given in support of these formulæ, and the percentage of each molecule present in the mixture is stated in each case. The following new analyses, by Dittrich and Noll, are given of tourmaline: I, bottle-green crystals from Brazil (D 3·064; $a:c=1:0\cdot4480$; optical determinations are also given); II, black crystals from Pierrepont, New York (D 3·120); III, black crystals from Andreasberg, Harz (D 3·250; $a:c=1:0\cdot4523$):

	SiO_2	TiO_2	B_2O_3	Al_2O_3	Fe_2O_3	FeO	MnO	CaO	Na_2O	Li_2O	K_2O	H_2O	F	Total
I.	37·74	—	11·54	38·43	1·58	1·93	1·25	0·06	0·60	2·37	1·66	0·47	3·21	101·97
II.	33·86	0·70	11·46	22·91	2·56	0·98	—	11·06	8·94	1·19	—	0·29	2·99	99·77
III.	34·01	0·61	10·89	23·80	4·87	13·57	0·12	0·42	0·58	2·93	0·10	0·20	2·92	99·33

The material from Andreasberg is richer in iron than any other tourmaline (containing 54% of the iron molecule), and here the crystallographic axis c is slightly longer. L. J. S.

Ægirite-like Pyroxene and Crocidolite from Golling, Salzburg. RICHARD DOHT and CARL HLAWATSCHE (*Verh. Geol. Reichsanst. Wien*, 1913, 79—95).—The well-known "sapphire-quartz" from Mooseck, near Golling, owes its blue colour to enclosed crocidolite. It is found in a gypsum quarry, and occurs in veins in a mixture of dolomite, chalybite, and steatite, with associated hematite, limonite, crocidolite, and an ægirite-like mineral. The last of these has the form of green radially-fibrous aggregates, and is shown by anal. I to contain much of the jadeite molecule, $\text{NaAlSi}_3\text{O}_6$, in addition to the ægirite molecule, $\text{NaFeSi}_2\text{O}_6$. The crocidolite forms loose, fibrous masses; D about 3·20; analysis II is near to that of "abrichanite" from Scotland:

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	CaO	MgO	Na_2O	K_2O	H_2O	Total
I.	52·61	8·51	22·22	1·47	trace	1·38	0·08	13·60	0·46	0·37	109·79
II.	56·71	2·33	14·70	7·60	—	—	9·62	5·42	0·57	3·69	100·49

L. J. S.

Composition and Origin of Alkaline Rocks. CHARLES H. SMYTH, jun. (*Amer. J. Sci.*, 1913, [iv], 36, 33—46).—The average composition of all igneous rocks, as deduced by F. W. Clarke, is quoted under I, and the average of twenty-three analyses of alkaline syenites is given under II. The latter shows more alkalis and alumina and less lime and magnesia:

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Total
I.	61·82	0·75	15·51	2·67	3·45	—	4·02	4·96	3·51	3·04	0·27	100·99
II.	62·48	0·56	18·07	2·24	2·31	0·08	0·97	2·57	5·68	5·02	0·14	100·00

The alkaline rocks are much rarer (less than 1% of the whole) and more local in their occurrence than the common type of sub-alkaline rocks. Further, they are characterised by the presence of the rarer elements lithium, glucinum, cerium, yttrium, zirconium, uranium, and thorium, and of the "mineralisers," fluorine, chlorine, and sulphur (as SO_3). It is maintained that these rocks have been derived from the more common magma by differentiation, and that this has been largely effected through the agency of the "mineralisers."

L. J. S.

The Meteorite of St. Michel, Finland. LEONHARD H. BORGSTRÖM (*Bull. Comm. Géol. Finlande*, 1912, No. 34, 1-49).—Two stones weighing 10 kg. and 7 kg. fell on July 12th, 1910. Analyses of the metallic portion extracted by copper-ammonium chloride and of the stony portions soluble and insoluble in hydrochloric acid give the following as the bulk composition:

Fe.	Ni.	Co.	Cu.	P.	S.	SiO_2 .	TiO_2 .	Al_2O_3 .
11.71	1.16	0.13	0.01	0.03	2.22	39.52	0.02	3.31
Cr_2O_3 .	FeO .	MnO .	CaO .	MgO .	K_2O .	Na_2O .	Total.	
0.66	13.44	0.41	1.64	24.60	0.13	1.32	100.26	

corresponding with the mineral composition: nickel-iron, 8.71; schreibersite, 0.51; troilite, 6.11; chromite, 0.82; olivine, 43.22; bronzite, 26.25; plagioclase, 14.63%.

L. J. S.

The Binda Meteorite. CHARLES ANDERSON and JOHN C. H. MINGAYE (*Records Australian Museum*, 1913, 10, 49-52).—This stone was found near Binda, Georgiana Co., New South Wales, on June 5th, 1912, and, being perfectly fresh, it is probably connected with the meteor seen on May 25th. The weight was stated to be 12 lbs., and two fragments of 5 lbs. $13\frac{1}{2}$ ozs. and 4 lbs. $6\frac{1}{2}$ ozs. are preserved. The crust is in two layers: an outer brilliant black crust showing lines of flow, and readily detachable from the under dull, black layer. The material is friable and holocrystalline in structure, with no chondrules. Anorthite, hypersthene, chromite, and specks of nickel-iron were identified under the microscope. D 3.25. Analysis gave:

SiO ₂ .	Al ₂ O ₃ .	FeO.	Fe.	FeS.	MnO.	Cr ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.			
50.50	8.84	15.29	0.45	0.96	0.51	0.75	6.15	16.15	0.28	0.13			
CuO.	V ₂ O ₅ .	P ₂ O ₅ .	C.	H ₂ O (116°).	BaO.	SrO.	NiO.	CoO.	CO ₂ .	Cl.	SO ₃ .	F.	Total.
trace	0.01	0.03	0.07	0.10							absent		100.22

absent

L. J. S.

Analytical Chemistry.

Analysis of Combustible Gases by Explosion. ENRIQUE HAUSER (*Anal. Fis. Quim.*, 1913, 11, 280—286).—A proportion of 8.33% of methane ensures that the combustion of nitrogen is too slight to cause an appreciable error. For exact work the oxides of nitrogen are absorbed by a known volume of water, the solubility of carbon dioxide being calculated and allowed for. G. D. L.

An Apparatus for Gas Analysis. T. S. AGRAZ (*Zeitsch. anal. Chem.*, 1913, 52, 418—419).—The apparatus consists of a cylindrical tube. The tube has a capacity of 100 c.c., and is divided to 0.1 c.c. At the upper end the tube carries a stopcock, to which is sealed a tube bent downwards. For the passage of electric sparks platinum wires are fixed below this stopcock.

At the lower end of the tube two side-tubes with stopcocks are attached; one serves for the introduction or withdrawal of gases or liquids, the other is attached by caoutchouc tubing to a movable globular reservoir. The eudiometer is supported by a solid wooden foot loaded with lead. L. DE K.

A New Calorimeter Bomb. SAMUEL W. PARR (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 389—393).—In this oxygen bomb for calorimetric use the platinum lining is replaced by an alloy composed of nickel, copper, tungsten, and chromium with smaller and more or less adventitious amounts of manganese, aluminium, titanium, boron, and silicon. This alloy is practically unaffected by the acids (nitric, sulphuric) which may form during the combustion.

A rubber gasket for sealing the bomb is substituted for the leaden one; in order to protect the rubber from being burnt a shoulder of massive metal is interposed between the rubber gasket and the inner chamber. The same principle is carried out in closing the main opening of the bomb and in closing the valve through which oxygen is admitted. L. DE K.

Some Tests on a New Calorimeter Bomb. RICHARD H. JESSE, jun. (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 233—236).—The new alloy bomb devised by Parr (preceding abstract) has been successfully tried with sugar and benzoic acid. In these combustions the method of adiabatic calorimetry devised by Richards has been used (*A.*, 1905, ii, 677; 1907, ii, 604). L. DE K.

Litmus Paper as a Quantitative Indicator of Reaction. GEORGE S. WALPOLE (*Biochem. J.*, 1913, 7, 260—267).—The reaction of a solution is indicated by the colour of a piece of litmus paper immersed in excess of the fluid until no further change can be observed. The correction for neutral salts, if present, is a small

one. When, however, a drop of the fluid is placed on litmus paper, the colour changes are influenced by glazing of the paper, the actual effect of the reaction of the material in the paper on the solution used, the reaction inertia of the paper, the effect of exposure to air, and the liberation of indicator from the paper. Determinations of reaction when proteins and their decomposition products are present are very difficult with litmus paper. The same phenomena are even more marked with litmus tincture.

W. D. H.

Some Applications of the Hydrogen Electrode in Analysis, Research, and Teaching. JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1913, 35, 847—871).—An account of the value of the hydrogen electrode as an indicator in titrations. Curves are given representing the titration of a number of acids, bases, and salts, and attention is drawn to the fact that such curves supply the only generally trustworthy test as to the suitability of an indicator. It is also shown how magnesium may be rapidly estimated in the presence of calcium by following the hydroxyl ion concentration when sodium hydroxide solution is gradually added, and how, with an unattackable electrode in place of the hydrogen electrode, it is possible to follow the course of oxidation and reduction reactions.

D. F. T.

Electrometric Determination of the Concentration of Hydrogen Ions in Biological Fluids. KARL A. HASSELBALCH (*Biochem. Bull.*, 1913, 2, 367—372).—In the electrometric method for the estimation of hydrogen ion concentration it is necessary that the electrode and the liquid should be saturated with hydrogen without any alteration in the hydrogen ion concentration of the liquid. In biological fluids containing volatile acids (or bases) this is a difficulty which can be overcome by leading a current of pure hydrogen saturated with moisture through the vessel containing the electrode until the latter is saturated with hydrogen. The liquid to be investigated is then led into the vessel, so that the electrode reaches into it for a certain depth. By shaking the vessel, the establishment of diffusion equilibrium between liquid and hydrogen, and attainment of constancy in the measured potential are accelerated. This constancy, however, is obtained by the loss of part of the volatile acid (or base) from the liquid to the hydrogen, and would therefore indicate an incorrect reaction. The liquid is next renewed without changing the gas mixture round the electrode, and shaking is repeated; electromotive constancy is thus reached without any appreciable alteration in the original fluid.

W. D. H.

Quantitative Relations in Capillary Analysis. HANS SCHMIDT (*Biochem. J.*, 1913, 7, 231—248).—Diluted acids produce a ring system when dropped on blotting paper, the acid remaining behind the water. The radius of the coloured circle produced by

the acid is connected with the concentration by an exponential equation. Various other mathematical details are given.

W. D. H.

Use of Saponin [for Removing Precipitates]. C. BUNGE (*Pharm. Zentr.-h.*, 1913, 54, 616).—In quantitative work it is often troublesome to remove the last traces of finely divided precipitates from the beaker. Addition of a drop of saponin solution to the rinsings overcomes this difficulty.

L. DE K.

Substitute for Platinum. LUD. KOPA (*Chem. Zeit.*, 1913, 37, 754).—The author recommends rods made of quartz glass (2–3 mm. in diameter) as a substitute for platinum wire in the usual flame tests.

L. DE K.

Physiology of the Thyroid. I. Methods for Estimating Iodine in Organic Substances. F. BLUM and R. GRUTZNER (*Zeitsch. physiol. Chem.*, 1913, 85, 430–470).—In order to determine the question whether thyroid protein circulates in the blood, a certain method of detecting organically-bound iodine is necessary. A separation of these compounds from any potassium or other iodides can be accomplished by the use of acetone; it was found that 80% of acetone coagulates all proteins, and leaves alkaline iodine in solution. The estimation of very small quantities of iodine in the coagulum is not attended with any difficulty.

W. D. H.

Estimation of Sulphur in Pyrites. WALTER S. ALLEN and HOWARD B. BISHOP (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 33–51).—1.3736 Gram of the ore is treated with 10 c.c. of a mixture of 2 parts of bromine and 3 parts of carbon tetrachloride. After fifteen minutes 15 c.c. of strong nitric acid are added, and after a while the whole is evaporated to dryness on a steam-bath. The residue is then again evaporated with 10 c.c. of hydrochloric acid to render silica insoluble. After moistening with 4 c.c. of hydrochloric acid and adding 100 c.c. of hot water, 0.2–0.3 gram of aluminium powder is added so as to reduce the ferric iron to the ferrous state, which is the chief feature in the process.

To the filtrate and washings are now added another 6 c.c. of hydrochloric acid (D 1.2), and then sufficient water to make up to 1 litre. The sulphuric acid is precipitated, in the cold, by adding at the rate of 5 c.c. per minute 125 c.c. of 5% barium chloride solution. The barium sulphate which is free from iron is then collected with the usual precautions.

L. DE K.

Estimation of [Combined] Sulphuric Acid in Wines. KARL VON DER HEIDE (*Zeitsch. anal. Chem.*, 1913, 52, 440–451).—The author having noticed that the result of the estimation of sulphates in wines is always higher when the acid is estimated after burning off the organic matters, has carried out a large number of experiments in order to elucidate the matter. The conclusions arrived at

are as follows: The higher result obtained when testing the ash is due to an oxidation of sulphur dioxide during the ashing process or to the presence of organic sulphur compounds; there is no danger of sulphuric acid being absorbed from the gas employed. The matter is not without significance, and it is finally recommended to estimate the acid by direct precipitation with barium chloride, after boiling off any sulphur dioxide with hydrochloric acid in a current of carbon dioxide.

L. DE K.

Apparatus for Nitrogen Estimation. O. WENTZKI (*Zeitsch. angew. Chem.*, 1913, 26, 400).—Instead of measuring the nitrogen obtained in a nitrogen estimation in the azotometer itself, a special measuring tube is attached to the azotometer in such a way that the nitrogen can be readily transferred to it, and its volume measured over water.

T. S. P.

Detection of Nitric Acid in Fruit Juices containing Added Water. ROBERT COHN (*Zeitsch. öffentl. Chem.*, 1913, 19, 223—226. Compare this vol., ii, 528).—The author finds that the ordinary diphenylamine-sulphuric acid test is capable of detecting the presence of as little as 2 mg. of nitric acid (N_2O_5) in 1 litre of fruit juice; smaller quantities may be detected when the reagent contains sodium chloride, but in view of the fact that traces of nitric acid are found in pure fruit juices, this more sensitive test may be of some disadvantage in detecting the presence of nitric acid introduced with the added water. Of course, a negative reaction with the test does not definitely indicate the absence of added water.

W. P. S.

Catalytic Acceleration of the Reduction of Nitrates by Schloesing's Method. RUDOLF HAC (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 207—208).—In Schloesing's process (boiling the nitrate with ferrous chloride and hydrochloric acid and measuring the volume of nitric oxide evolved) the reaction may be much accelerated by addition of about 0.1 gram of molybdic acid before introducing the ferrous chloride and the acid.

L. DE K.

Modification of Marsh's Process for the Estimation of Arsenic. ALEXANDRE HERBERT (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 213—215).—The process is that of judging the amount of arsenic from the intensity of the arsenical mirror, but differs from the usual method in the way the hydrogen is generated. The author introduces into the generating flask a thin layer of pure mercury and 40 c.c. of dilute sulphuric acid (10 vol. %), also the liquid containing the arsenic (say, minute fractions of a mg.). The air having been displaced by a current of carbon dioxide, 100 grams of liquid sodium amalgam are introduced drop by drop, this operation occupying about half an hour. The slow but steady evolution of hydrogen then carries off the arsenic hydride, which is passed through a red-hot tube as usual. Finally, the flask is swept out by a very slow current of carbon dioxide.

L. DE K.

Accurate Estimation of Arsenic Based on the Gutzeit Test. WALTER S. ALLEN and RALPH M. PALMER (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 9—17).—In order to obtain accurate results with the well-known Gutzeit stain test, ferric chloride, reduced by means of stannous chloride, should be present. The standard stains should be made with ferrous and stannous chlorides present in the solution in approximately the same amounts as are found in the samples analysed. Iron should be added to all samples which do not contain it.

L. DE K.

Volatility of Arsenious Chloride. JOHN T. D. HINDS (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 227—231).—A series of experiments leading to the following conclusions:

The quantity of arsenious arsenic lost on boiling in hydrochloric acid solution is a function of the concentration both of the arsenic and of the acid. When the concentration of the acid exceeds that of the arsenic, the fraction of the arsenic volatilised approaches a constant value. With the concentrations usually employed in qualitative analysis, the loss of arsenic on boiling the solution to half its bulk may be disregarded.

L. DE K.

Titration of Arsenic Acid. ALAN W. C. MENZIES and PAUL D. POTTER (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 367—371).—Unsatisfactory results are obtained by direct titration of arsenic acid with standard alkali, but the process is much improved by adding barium chloride, thus liberating hydrogen chloride. A quantity of arsenic acid solution likely to require 30—40 c.c. of normal alkali is mixed with 15 c.c. of saturated barium chloride solution, and the whole is diluted to 250 c.c. and boiled for a few minutes. When cold, the liquid is titrated with *N*-sodium hydroxide (containing a little barium hydroxide). The alkali is added with stirring until the precipitate becomes slow in redissolving. After thorough stirring and removing any matter from the walls of the beaker, the liquid, which appears lustrous with fine crystals, is now titrated further, using phenolphthalein as indicator.

The alkali is preferably checked against pure arsenic acid in the manner described.

L. DE K.

Detection of Infinitesimal Traces of Boron by means of Tincture of Mimosa Flowers. LUCIEN ROBIN (*Bull. Soc. chim.*, 1913, [iv], 13, 602—606).—The principle of the method has already been described (*A.*, 1904, ii, 445), and the present paper gives details for the use of the tincture instead of paper dyed with the tincture as a reagent for boron. By the method now described, as little as 0.00027 mg. of boric acid can be detected. The reaction is slightly affected by sodium phosphate, but not by other inorganic salts tried. In presence of organic salts, the latter must be removed by ignition before the reagent is applied. Directions for its use in the detection of boron in wines and milk are also given.

T. A. H.

Estimation of the Organic Substance in Clays. F. EHRENBERG, C. DIEBEL, and H. VERKENSTEDT (*Zeitsch. anal. Chem.*, 1913, 52, 408—418).—The authors come to the same conclusion as previous investigators, that the moist combustion methods (use of chromic acid or alkaline permanganate) are not so trustworthy in clay analysis as the combustion with copper oxide. L. DE K.

Apparatus for the Estimation of Air in Liquid Carbon Dioxide. O. WENTZKI (*Zeitsch. angew. Chem.*, 1913, 26, 376).—The apparatus consists of a burette provided with a tap at the top and a three-way tap at its lower end. A side-tube above the three-way tap is connected with a reservoir containing potassium hydroxide solution. A measuring bulb is placed immediately below and in connection with the three-way tap, and is connected with a mercury reservoir. The carbon dioxide is admitted from the cylinder into the measuring bulb, and, when this is filled, the gas is shut off (a second three-way tap is provided between the apparatus and the cylinder, one arm of this tap being connected with a bubbling-flask, so that the rate of flow of the gas may be ascertained) and the gas is caused to pass slowly into the burette by raising the mercury reservoir, the burette having been filled previously with potassium hydroxide solution; the reservoir for the latter solution also serves as a levelling vessel when the volume of the residual air is read off. W. P. S.

Detection and Estimation of Exceedingly Minute Quantities of Carbon Dioxide. HERBERT N. MACCOW and SHIRO TASHIRO (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 361—366; *Amer. J. Physiol.*, 1913, 32, 137—145).—The gaseous mixture (air, for instance) is brought into contact with a drop of clear barium hydroxide solution in a special apparatus, and if a cloud should form, it is found by trial what volume of the gas is still capable of just showing the reaction within ten minutes. The minimum volume of carbon dioxide required must be determined by a previous experiment. L. DE K.

Estimation of Carbon Dioxide. LUDWIG W. WINKLER (*Zeitsch. anal. Chem.*, 1913, 52, 421—446).—The author upholds the accuracy of his process published in 1903 (*A.*, 1904, ii, 215), in which the expulsion of the carbon dioxide is much accelerated by the addition of zinc to the acid liquid; the gases evolved are first dried over calcium chloride, and then absorbed in a weighed Liebig's potash apparatus. The process is applicable to the analysis of carbonates as well as to natural waters.

For the estimation of carbon dioxide in the air, the time-honoured method of Pettenkofer is again recommended (action of lime water, titrating the excess with phenolphthalein as indicator). It is recommended that the bottle should be filled by applying suction, and not by blowing in the air by means of bellows. A convenient arrangement for this purpose is described. L. DE K.

The Use of the Fontactoscope for the Estimation of the Emanation Content of Spring Water. CARL ENGLER and HERM. SIEVEKING (*Physikal. Zeitsch.*, 1913, 14, 658).—Polemical against Hammer and Vohsen (this vol., ii, 622). J. F. S.

Detection of Potassium with Tartaric Acid. HANS RECK-LEBEN (*Zeitsch. angew. Chem.*, 1913, 26, 375—376).—To the solution to be tested for potassium is added a moderately concentrated sodium hydrogen tartrate solution, and the mixture is stirred; if no crystals appear on the sides of the vessel containing the mixture, especially where the stirring rod has touched the side, a drop of the mixture is transferred to a watch-glass and stirred with a drop of 10% potassium chloride solution. A minute quantity of the crystals thus obtained is introduced into the original mixture, and stirred. A crystalline deposit will be obtained if potassium is present. A mixture of sodium acetate and tartaric acid may be used in place of sodium hydrogen tartrate, but the tartaric acid must be in excess, as potassium hydrogen tartrate is soluble in an excess of sodium acetate. W. P. S.

Rational Analysis of Sodium Nitrate. The Use of the Devarda Method versus the Misleading "Refraction" Method. WALTER S. ALLEN (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 19—31).—The custom of estimating the moisture, sodium chloride, sodium sulphate, and insoluble matter, and then taking the sodium nitrate by difference ("refraction"), is shown to be quite erroneous, as they are by no means the only impurities (potassium, calcium, magnesium, perchlorate, etc.).

Hence, the estimation must be carried out by conversion of the nitric acid into ammonia and titrating the latter with methyl-red as indicator. For the conversion into ammonia, Devarda's alloy (aluminium, 45; copper, 50; zinc, 5 parts) is recommended in alkaline solution. L. DE K.

Spectroscopic Method for the Estimation of Lithium. W. W. SKINNER and W. D. COLLINS (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 453—468).—The authors state that satisfactory spectroscopic estimations of lithium may be obtained according to the processes of Ballmann, Bell, or Foehr when applied to the alkalis extracted with amyl alcohol by the Gooch method.

Contrary to Ranzoli's statement, the quantitative spectroscopic estimation is not to be preferred to the gravimetric estimation (amyl alcohol process) if the lithium is present in weighable quantities. A rough spectroscopic examination is recommended in testing for alkalis, lithium, barium, strontium, and calcium, so as to serve as a guide to the proper procedure in analyses. L. DE K.

Qualitative Analysis of the Calcium Group. RICHARD EDWIN LEE and F. L. MICKLE (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 257—278).—Barium, calcium, and strontium may be separated

completely from magnesium by precipitation with ammonium carbonate (200 grams of the normal salt, 500 c.c. of ammonia, D 0.90, water up to a litre) in presence of a sufficiency of ammonium chloride in the cold and in slightly ammoniacal solution. Barium may then be separated from the other two metals by precipitating the hot acetic acid solution of the carbonates with potassium chromate. From the filtrate the strontium may then also be obtained as chromate on adding an equal volume of 95% alcohol. To the filtrate is added some more potassium chromate and also more alcohol to completely remove any strontium. The filtrate now containing only the calcium is diluted with twice its volume of water, and precipitated hot with ammonium oxalate. The precipitates may then be further identified in various ways, for instance, by means of the spectroscope. L. DE K.

Estimation of Magnesium by Precipitation as Magnesium Ammonium Phosphate or Arsenate. MAX WUNDER and C. SCHULLEZ (*Ann. Chim. anal.*, 1913, 18, 221—222).—In order to obtain satisfactory results, the respective precipitates should be collected on a Gooch filter and washed with water containing 3.5% of ammonia; the precipitate is then dried at a temperature not exceeding 100°. For the conversion into the pyro-compounds the Gooch crucible is placed into a large porcelain crucible, the bottom of which is lined with asbestos. Heat is at first applied with a Bunsen burner for three-quarters of an hour, then the crucible is heated over a Teclu burner, and finally on the blowpipe. Both crucibles should be covered during the operation. L. DE K.

Rapid Estimation of Magnesia in Limestone by means of the Hydrogen Electrode. JOEL H. HILDEBRAND and HERBERT S. HARNED (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 217—225).—The process is based on the fact that if to a mixture of a neutralised solution of calcium and magnesium chlorides is added normal alkali the magnesium is precipitated first, the end-point being observed by a further rise in potential. The apparatus required, accompanied by a curve, is described and figured in the original paper. L. DE K.

The Roasting of Zinc Sulphide Precipitates and a New means of Rapid Coagulation of these Precipitates from Acid Solution. (Mutual Precipitation of Two Colloids, Applied to an Analytical Problem.) KARL BORNEMANN (*Zeitsch. anorg. Chem.*, 1913, 82, 216—239).—Zinc sulphide may be directly ignited to oxide without separation from the filter paper if a shallow, open, porcelain crucible is used, ignited over a full Bunsen flame, or if, with a platinum crucible, the temperature does not exceed dull redness. When the filter paper is completely burnt, the precipitate must be heated strongly to decompose zinc sulphate. This must be above 935°, best in an electric furnace. Ignition in a well-closed crucible for fifteen to twenty minutes over a Teclu or Meker burner is sufficient.

The precipitation of zinc sulphide is greatly assisted by the presence of a second colloid, especially by sulphur. This is best carried out by precipitating in acetic or chloroacetic acid solution in presence of sodium hydrogen sulphite, passing hydrogen sulphide briskly. The precipitate coagulates well, and is washed on the filter with 0.5—1% ammonium nitrate. A slight turbidity remains in the solution, but this is due only to sulphur.

The presence of sulphur is without any harmful influence on the separation from iron, cobalt, or nickel. With strongly acid dilute solutions, the separation from iron is practically complete.

C. H. D.

Volumetric Estimation of Traces of Zinc. ANGEL DEL CAMPO Y CERRAN (*Anal. Fis. Quim.*, 1913, 11, 287—293).—The blue coloration given by ammoniacal zinc solutions with resorcinol is discharged by alkali stannite, or, if acidified, by stannous chloride solution. A method of volumetric estimation is based on these facts.

G. D. L.

Separation of Cadmium from Zinc. W. D. TREADWELL and K. S. GUITERMAN (*Zeitsch. anal. Chem.*, 1913, 52, 459—469).—*By hydrogen sulphide.*—The solution should contain free sulphuric acid to the extent of 4—5 normal. The cadmium is precipitated as sulphide in the hot solution, and the gas passed until the liquid is cold. If large excess of zinc is present, the precipitate is redissolved in hot dilute hydrochloric acid (1:1), evaporated with a slight excess of sulphuric acid, and reprecipitated with hydrogen sulphide.

By Electrolysis.—About 1 gram of the mixed chlorides or sulphates is mixed with 8 grams of potassium oxalate, 2 grams of ammonium oxalate, and 0.3—0.5 gram of oxalic acid, and the solution electrolysed with gauze electrodes at 70—80° for four to five hours for each 0.1 gram of cadmium present; current, 0.05 ampère; tension, 1.4—1.6 volt. From 0.04 to 0.20 gram of cadmium may be estimated in the presence of fifty times the amount of zinc by adding 5 grams of sodium hydrogen sulphate, and electrolysing in the cold with a quick rotating electrode; a gauze cathode is unsuitable here. 0.2 Gram of cadmium is deposited within thirty to sixty minutes.

L. DE K.

Copper Content of Distilled Water. EMIL ABEL (*Zeitsch. Elektrochem.*, 1913, 19, 477—480).—During studies on the velocity of the reaction between hydrogen peroxide and sodium thiosulphate (*A.*, 1908, ii, 26) the author in one set of determinations obtained values for the velocity constant which were far higher than any previously obtained. Investigation showed that the high values were due to the presence of mere traces of copper in the distilled water which had catalysed the reaction. The author has devised a method, depending on the velocity of reaction between hydrogen peroxide and sodium thiosulphate, by which the amount of copper in distilled water can be estimated. In an experiment the author finds 0.000038% Cu present in the distilled water, whilst by

evaporating 80 litres of the water and weighing the residue the value 0.000040% Cu was obtained.

J. F. S.

Estimation of Copper in Cupriferous Pastes. PHILIPPE MALVEZIN (*Ann. Chim. anal.*, 1913, 18, 220).—0.1 Gram of the sample is calcined, the residue dissolved in nitric acid, and diluted to 20 c.c. Of the filtrate 10 c.c. are mixed with 2 c.c. of ammonia and made up to 20 c.c.; if necessary the solution is filtered, and to 10 c.c. of the filtrate another 1 c.c. of ammonia is added and the solution is now titrated with formaldehyde-sulphurous acid until colourless.

This reagent is prepared by passing sulphur dioxide through commercial "formalin." The solution is then standardised as follows: One gram of metallic copper is dissolved in nitric acid and diluted to 100 c.c.; 1 c.c. of this is then mixed with 2 c.c. of ammonia and 1 c.c. of water, and titrated.

L. DE K.

Rapid Process for the Estimation of Copper in Roasted Pyrites. HERMANN KOELSCH (*Chem. Zeit.*, 1913, 37, 753).—Ten grams of the finely powdered sample are heated to boiling with 6–7 grams of sodium hypophosphite and 40 c.c. of hydrochloric acid (D 1.16). Without filtering, the liquid is diluted with 100 c.c. of hot water, and then mixed with 50 c.c. of sodium sulphide solution (40 grams per litre). After shaking a few times the precipitate soon settles, and is then collected and washed with hot water. The filter and contents are treated in a porcelain crucible with nitric acid, which is then expelled by evaporation with sulphuric acid. After dissolving the residue in 100 c.c. of water, the copper is deposited electrolytically; or the precipitate may be dissolved in 10 c.c. of nitric acid, and heated until red fumes cease; the last traces of nitrous compounds are destroyed by addition of urea. The copper may then be estimated by first adding slight excess of ammonia and then a slight excess of acetic acid. Potassium iodide is added, and the iodine liberated (which represents the copper) titrated with thiosulphate.

L. DE K.

Iodometric Estimation of Copper. M. EMMANUEL POZZI-ESCOTT (*Ann. Chim. anal.*, 1913, 18, 219).—In the analysis of copper products the iodometric estimation is interfered with by nitrous compounds, which also liberate iodine from potassium iodide. The author overcomes this difficulty by adding excess of urea. The liquid is then mixed with excess of ammonia, the residue freed from copper by redissolving in dilute sulphuric acid and reprecipitation with ammonia, the united liquids are acidified with acetic acid, and after adding potassium iodide, the iodine liberated is titrated as usual.

L. DE K.

Detection and Separation of Aluminium and Glucinum by the Action of Amyl Alcohol on the Nitrates. PHILIP E. BROWNING and SIMON B. KUZIRIAN (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 87–90).—The process is based on the solubility of

glucinum nitrate in amyl alcohol, when not more than 0.1 gram of the same dissolved in a few drops of water is boiled with 10 c.c. of amyl alcohol until the water has evaporated. In these circumstances aluminium nitrate is insoluble.

As a quantitative method the separation may be trusted to be accurate within about 1 mg. after a double treatment with amyl alcohol. In any case the process may be recommended for the preparation of glucinum nitrate free from aluminium. The nitrate may be recovered from its amyl alcohol solution by repeated shaking with water.

L. DE K.

Influence of Hydrogen Sulphide on the Quantitative Precipitation of Certain Hydroxides by Sodium Thio-sulphate. RUDOLF HAC (*Eighth Inter. Cong. App. Chem.*, 1912, 1, 205—206).—An adverse criticism of Chancel's process for the separation of iron and aluminium by boiling the solution with sodium thiosulphate. The author states that the alumina is but imperfectly precipitated, although a complete precipitation will take place if a current of hydrogen sulphide is passed simultaneously. In that case, however, some ferrous iron is also thrown down.

Salts of glucinum are not precipitated on boiling with thio-sulphate unless a current of hydrogen sulphide is passed for at least two hours. Thorium salts are quantitatively precipitated by simply boiling with thiosulphate. Ceric salts are not precipitated, not even by the simultaneous action of hydrogen sulphide.

L. DE K.

Reduction of Ferric Salts and Filtration by Potassium Permanganate. ANDRÉ LECLÈRE (*J. Pharm. Chim.*, 1913, [vii], 7, 587—589).—The solution is acidified with 1 or 2 vols. % of sulphuric acid, a sufficiency of granulated zinc is added, also a piece of platinum wire. In order to render the ferrous sulphate formed more stable, 2—3 grams of ammonium sulphate are also added, and the whole is then heated in an Erlenmeyer flask, the neck of which is closed by a small funnel, for an hour at boiling heat. When all the iron has been reduced, the liquid is filtered through glass wool, and the residue is well washed. There is no fear of oxygen being absorbed, even if the filtration should have to be repeated before titrating with permanganate.

L. DE K.

Detection and Estimation of Nickel by means of α -Benzil-dioxime. FREDERICK W. ATACK (*Analyst*, 1913, 38, 316—321).—An alcoholic solution of α -benzildioxime, to which a little ammonia has been added, constitutes a delicate reagent for the detection of nickel owing to the formation of a red precipitate. When applying the reaction quantitatively, the solution, which should not contain more than 0.025 gram of the metal, is rendered alkaline with ammonia, an excess of the warm solution of the reagent is added with stirring, and the whole heated on the water-bath until the precipitate has coagulated. After remaining for an hour in

a warm place, the precipitate is collected on counterpoised filters, washed with warm 50% alcohol, then with hot water, and finally dried at 110°. It contains 10.93% of nickel.

The detection and estimation is not affected by cobalt, ferric iron (to which sodium citrate has been added), manganese, (in presence of a slight excess of acetic acid), zinc and magnesium (in presence of ammonium chloride), and chromium (in presence of ammonium tartrate).

The method is interfered with by the presence of nitrates, which should therefore be expelled by evaporation with sulphuric acid.

L. DE K.

Use of Hydrazine and Some of its Derivatives in the Gravimetric Estimation of Chromium. JOSEF HANUS and T. LUKAS (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 209—212).—Hydrazine, but preferably thiosemicarbazide, is stated to be a very suitable reagent for the estimation of chromium. To the neutral solution of the chromate is added an excess of ammonium chloride (at least 5 mols. to 1 mol. of chromate), then an excess of the reagent, and the whole is heated to boiling. The chromium is precipitated rapidly as hydroxide, which is then collected and treated as usual.

In the presence of iron and aluminium the mixture is oxidised with hydrogen peroxide in ammoniacal solution; sometimes it is advisable to redissolve the drained precipitate and repeat the operation. The mixed filtrates are then neutralised with hydrochloric acid, and precipitated as directed.

L. DE K.

Volumetric Estimation of Chromium in the Presence of Iron. ALBIN KURTENACKER (*Zeitsch. anal. Chem.*, 1913, 52, 401—407).—The solution of the mixed chlorides is introduced into a 250 c.c. flask, excess of bromine water is added, and then a large excess of aqueous potassium hydroxide. The mixture is now heated for half an hour on the water-bath with frequent shaking; by that time the iron has completely separated as hydroxide, whilst the chromium is converted into chromate. When cold, water is added to the mark, and, after shaking, the supernatant liquid is poured through a dry filter. One hundred c.c. of the filtrate are treated with dilute sulphuric acid until separation of bromine sets in, when 20 c.c. of 30% solution of potassium hydrogen sulphate are added, and the whole boiled for five minutes to expel the bromine. In case of doubt, another 10 c.c. of the hydrogen sulphate are added, and the boiling is repeated. When cold, the chromate is estimated iodometrically, as usual.

The iron precipitate is well washed, dissolved in dilute hydrochloric acid, and also titrated in the usual manner.

L. DE K.

Assay of Tin, Solder, and Lead Dross by Electrolysis. I. BERTIAUX (*Ann. Chim. anal.*, 1913, 18, 217—219).—Five grams of the tin or 1 gram of the solder dross are fused in a porcelain crucible with three parts of sodium carbonate and 3 parts of

sulphur, the mass is extracted with water, and the filtrate made up to a definite volume, of which is then taken an aliquot part representing 1 gram of material (in the case of solder the whole of the filtrate is used). The solution containing the tin sulphide is evaporated to dryness with addition of 15 grams of ammonium sulphate on a sand-bath, the residue is oxidised with nitric acid, and then evaporated with 5 c.c. of sulphuric acid until acid fumes cease. The residue is taken up with water, and boiled with 30 c.c. of hydrochloric acid and 30 grams of ammonium oxalate. The tin is then deposited electrolytically in the author's apparatus; temperature 40°, current 1—3 ampere.

In order to estimate the lead in the undissolved sulphide (tin material), this, after being washed with water containing hydrogen sulphide, is boiled for half an hour with a mixture of 100 c.c. of copper nitrate solution (? strength), 4 c.c. of ammonia, and 80 c.c. of nitric acid (D 1.33). The filtrate and washings are made up to 300 c.c., and the lead is then deposited as usual as peroxide; current, 0.3—1 ampere, finally 1—1 ampere, to deposit the last traces of lead. When estimating lead in solder dross, 1 gram is treated with 100 c.c. of copper nitrate and 25 c.c. of nitric acid, diluted to 300 c.c., and electrolysed; current 1—0.3 ampere. The same process is used for lead dross.

L. DE K.

Assay of Tin Ores. H. MILOU and R. FOURET (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 373—385).—The ore (2 grams) is fused in a steel crucible with 10 parts of sodium peroxide for twenty minutes, the mass is dissolved in water, and treated with 70 c.c. of hydrochloric acid, which should give a clear solution. After heating at 90°, 4 grams of iron wire are introduced, which precipitates any arsenic, antimony, and copper, and reduces the tin to the stannous state. After half an hour, the liquid is filtered, and the residue well washed. After again warming to about 95°, 10 grams of granulated zinc are added, so as to precipitate the tin.

After pouring off the liquid through a funnel containing a little glass wool, and washing the residue, the latter (to which the glass wool is then added) is dissolved in about 30 c.c. of hydrochloric acid in a flask fitted with a doubly perforated rubber cork, carrying an inlet tube connected with a carbon dioxide generator, and an exit-tube. When, after heating, all the metal has dissolved, the exit-tube is closed until the contents have cooled. Two hundred and fifty c.c. of water free from air are now introduced, and the tin titrated with standard iodine with starch as indicator.

L. DE K.

Volumetric Estimation of Titanium. PORTER W. SHIMER and EDWARD B. SHIMER (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 445—451).—Reduction of titanium dioxide to sesquioxide by means of dilute sulphuric acid and zinc rods is very slow and often imperfect, but according to the authors complete reduction takes place within fifteen minutes by using a very long reductor filled with amalgamated zinc. This also reduces any iron present, so that the titanium cannot then be estimated with permanganate; a

standard solution of ferric ammonium-sulphate is, therefore, used with potassium thiocyanate as indicator. The operations should be carried out in an atmosphere of carbon dioxide. Titanium may be separated from vanadium by fusion with sodium carbonate and sulphur; from the fused mass the vanadium may be extracted with water. When testing pig-iron for titanium a large quantity may be dissolved in hydrochloric acid, when all the titanium will be found in the insoluble residue.

L. DE K.

Antimony Pentachloride as a Reagent for the Examination of Aromatic Hydrocarbons. SIEGFRIED HILPERT and LUDWIG WOLF (*Ber.*, 1913, 46, 2215—2218).—Antimony pentachloride dissolved in carbon tetrachloride gives characteristic reactions with many aromatic hydrocarbons. About 0.1 gram of the hydrocarbon is dissolved in 1' or 2 c.c. of the solvent, and a 30% solution of the reagent is added drop by drop. Pure benzene gives a yellow to orange coloration, but concentrated solutions deposit a pale additive compound. Commercial benzene, however, gives a dirty green colour and a dark precipitate, 0.3 mg. of thiophen per c.c. still responding to the test. Condensed hydrocarbons produce deeper colours. Naphthalene gives, in a few seconds, a dark lilac precipitate, indene gives a bluish dark-red precipitate at once, and anthracene forms an intense green precipitate. Phenanthrene gives a brown precipitate, but 8 mg. of anthracene in 1 gram of phenanthrene can be detected by the formation of the above green precipitate. Carbazole gives a light green precipitate, and may thus be distinguished from thiophen.

The detection of impurities in anthraquinone may be carried out by extracting a sample with a small volume of hot carbon tetrachloride and testing the extract for anthracene or carbazole in the above manner, and then applying the reagent to a solution of the less soluble quinone. Anthraquinone forms a cinnabar-red precipitate, whilst phenanthraquinone gives a deep red coloration, and traces of the latter may thus be detected. Diphenyl- and triphenyl-methane and fluorene also yield green additive compounds. The presence of methyl groups renders the colour more and more dark red. Nitro-, amino-, and carboxyl groups, however, have the opposite influence.

Carbon tetrachloride must be used as the solvent, for in chloroform solution less characteristic and even colourless products are obtained.

J. C. W.

Volumetric Estimation of Methoxy- and Ethoxy-groups. ALFONS KLEMENC (*Monatsh.*, 1913, 34, 901—912).—Zeisel's method of estimating alkoxy-groups has not found technical application, since alcoholic silver nitrate solutions must be employed, and the determination requires considerable time. The author has endeavoured to overcome these difficulties by leading the alkyl iodide, evolved in the usual manner, through a heated tube packed with a suitable material, the liberated iodine being subsequently titrated by means of sodium thiosulphate solution.

The apparatus consists of a small flask in which the decomposi-

tion is effected, and from which the alkyl iodide is driven by a current of carbon dioxide-free air through a reflux condenser, and thence through a small bubbler containing a suspension of red phosphorus in water. Thence the vapours pass into a hard glass decomposition tube about 25 to 28 cm. long and 1.2 cm. external diameter. The tube is drawn out at either end. The front end of the tube is packed with about 1 gram of 25% platinised asbestos, behind which is a roll of platinum foil formed by making a number of parallel cuts in a piece of foil and rolling it round an axis parallel with the line of the incisions. The remainder of the tube is filled with pumice held in position by a wad of asbestos. The narrowed end of the decomposition tube is connected by a ground joint with a tube which dips into a small vessel containing concentrated potassium iodide solution. The latter vessel is contained in an Erlenmeyer flask, on the bottom of which, is a layer of water; this communicates with the air through a Peligot tube.

In the actual determination it is important that the alkyl iodide should be driven into the decomposition tube mixed with as much air as possible. In normal cases, decomposition is complete in one-half to three-quarters of an hour.

At the conclusion of the decomposition, the liberated iodine is titrated in the ordinary manner. To determine the small quantity of iodine which is evolved in the form of hydrogen iodide, a considerable excess of potassium iodate is added; the solutions are allowed to remain for fifteen to thirty minutes, and the liberated iodine estimated with sodium thiosulphate. Since, however, small quantities of carbon dioxide are always present, partly dissolved in the water and partly obtained by the combustion of the alkyl iodide, it is necessary to carry out a blank experiment for this stage, and to deduct the iodine thus found from that obtained as above.

From a large number of experiments the author is led to the conclusion that the errors of his method are slightly greater than those of Zeisel's gravimetric estimation, and lie generally between +0.5% and -1.0%.

For the determination of the methoxy-group it is sufficient to fill the decomposition tube solely with pumice; with a tube filled in this manner, however, the values found in estimating ethoxy-groups are very low. The error is due to decomposition of ethyl iodide into ethylene and hydrogen iodide, and subsequent partial combination of the former with the liberated iodine with production of di-iodoethane. This error can be minimised, but not completely abolished, by packing the tube with platinum and platinised asbestos as described above, so that the hydrocarbon is completely oxidised.

H. W.

The Effect of Nitrotoluenes on the Determination of Glyceryl Trinitrate by means of the Nitrometer. C. G. STORM (*Eighth. Inter. Cong. App. Chem.*, 1912, 4, 117—125).—The determination of glyceryl trinitrate by the nitrometer is not

affected by the presence of pure di- or tri-nitrotoluenes; in the process, however, any mononitrotoluene becomes quantitatively converted into dinitrotoluene by the nitric acid liberated from the glyceryl trinitrate, thus decreasing the volume of gas produced. Analysis of unknown mixtures of glyceryl trinitrate with nitrotoluenes will therefore be trustworthy only if the amount of mononitrotoluene present is too small to cause an appreciable effect.

D. F. T.

Behaviour of Sugars with Diphenylamine and Hydrochloric Acid. H. T. B. RASMUSSEN (*Ber. deut. pharm. Ges.*, 1913, 23, 379—382).—The author has applied the reaction described by Jolles for the detection of levulose in urine (*A.*, 1909, ii, 1057) to a number of sugars, and finds that the ketoses give a deeper colour and in a shorter time than the aldoses. Furfuraldehyde gives a brownish-red coloration with diphenylamine and hydrochloric acid, which becomes dark green on shaking with ether. When hydrochloric acid is replaced by sulphuric acid, a gooseberry-red tint is produced. A table showing the colours given by solutions of various sugars at different concentrations and after various times of warming, is given in the original. The test is suitable for the detection of levulose in urine, but not for finding levulose or sucrose in presence of other sugars. For the detection of levulose in presence of dextrose by this means, the quantity of the latter must be known.

T. A. H.

Ivar Bang's Method for the Estimation of Sugar. ZENNOSHIN HATTA (*Biochem. Zeitsch.*, 1913, 52, 1—43).—As a result of detailed experimental investigation in each stage of Bang's method for the estimation of sugar, the author draws the conclusion that the deviations from the correct result may be influenced by three principal factors, namely, (1) the rate of titration; (2) the temperature of the copper solution at the time of reduction; (3) the auto-reduction of the sugar solution. It is not difficult to obtain fairly constant results by titrating at constant rate and at the same temperature. The deviations from constant results due to the first two factors are therefore not of great moment. The error due to the third factor will, however, vary with the amount of sugar in the solution, and tables are given showing corrections for this factor obtained by two different methods of calculation. The results thus obtained still show deviations from the correct values.

S. B. S.

Influence of Urea and Betaine on the Velocity of Hydrolysis of Sucrose by Hydrochloric Acid. WILLIAM E. CROSS and W. G. TAGGART (*Zeitsch. ver deut. Zuck-rind.*, 1913, 560—565).—It is proved that both urea and betaine have very little effect in retarding the velocity of hydrolysis of sucrose by hydrochloric acid at 28° or even at 20°. Consequently the use of these substances in analytical methods, which aim at determining the rotatory power of sucrose in acid solution, is unsafe, and the method is inapplicable for the analysis of molasses.

E. F. A.

New Test for the Detection of Saccharine Substances in Urine. ARDASHIR K. TURNER (*Chem. World*, 1913, 2, 202—203).—The test depends on the rise in temperature which takes place when urine is mixed with sodium hypobromite solution. If 5 c.c. of normal urine are added to 25 c.c. of hypobromite solution (2 c.c. of bromine dissolved in 23 c.c. of sodium hydroxide solution prepared by mixing 100 grams of sodium hydroxide with 250 c.c. of water) the increase in temperature of the mixture will be from 4° to 13·5°. Should the urine contain a sugar or glycerol, the rise in temperature may amount to 40°, this result being obtained in the case of a urine containing 10% of added dextrose. On keeping, the mixture deposits characteristic crystals, which appear to be sodium oxalate resulting from the oxidation of sugar or glycerol. Sugars, starch, and glycerol yield the same kind of crystals.

W. P. S.

The Hydrolysis of Levulosans and its Application to Plant Analysis. PH. L. DE VILMORIN and FERDINAND LEVALLOIS (*Bull. Soc. chim.*, 1913, [iv], 13, 684—691).—An examination of the behaviour of inulin towards various hydrolysing agents. The authors recommend the use of 5-sulphosalicylic acid at a concentration of 0·72 to 4·3 grams per litre, and at a temperature of from 80° to 100°, the results obtained being constant over a sufficiently wide period of time to avoid risk of error, and, furthermore, this acid has no effect on the subsequent estimation of the reducing sugars by Fehling's solution. Sulphuric and oxalic acids give figures which are too variable to serve as a basis for analysis. Acetic acid at a temperature of 80° and a concentration of 3—10% gives fairly concordant results, but this acid and its salts interfere with the subsequent determination of the sugars.

W. G.

Estimation of Crude Fibre and Cellulose. HERMANN MATTHIES and F. KÖNIG (*Arch. Pharm.*, 1913, 251, 223—245).—The authors have compared the "crude fibre" isolated from cinchona bark by the Henneberg-Weende, König, and Cross and Bevan processes, and find that of the three products that afforded by the Cross and Bevan process is the most satisfactory, and they describe in detail a modification of this process for general use. Full details are given in the original of the yields of "crude fibre" and "cellulose" obtained by these three processes, and of the behaviour of these products with various reagents (compare A., 1907, ii. 991).

T. A. II.

Volatility of Lactic Acid. EDWIN B. HART and J. J. WILLAMAN (*J. Amer. Chem. Soc.*, 1913, 35, 919—923).—In reply to Dox and Neidig (this vol., i, 236), who have criticised the authors' methods for the determination of the volatile acids of silage, the results of experiments are described which indicate that lactic acid is so little volatile in steam at 100° that the amount which passes over in the distillation of volatile acids from silage is insignificant. The higher results of Dox and Neidig in their experiments on the

volatility of lactic acid, may have been due to carbon dioxide in the water used or to volatile impurities in the lactic acid.

D. F. T.

Application of the Method of Estimating Tartaric Acid as Calcium Racemate to Solutions of Tartaric Esters. ANDRÉ KLING and E. GELIN (*Eighth. Inter. Cong. App. Chem.*, 1912, 1, 251—256).—For the estimation of tartaric acid, the process by precipitation as calcium racemate (Abstr., 1911, ii, 666) is again recommended. If tartaric esters are also present, the total amount of the tartaric acid may be estimated after saponification.

If ethyl hydrogen tartrate is present, the tartaric acid contained therein may be estimated by titration, allowance being made for any free tartaric acid. The result must then be multiplied by two.

L. DE K.

Detection and Estimation of Salicylic Acid in Fruit Juices. WALTER HEINTZ and R. LINPRICH (*Zeitsch. Nahr. Genussm.*, 1913, 25, 706—717).—The method depends on the fact that, under given conditions, light petroleum extracts a definite proportion of salicylic acid from its aqueous solution, and that on shaking the petroleum solution with dilute ferric chloride solution, the salicylic acid is obtained in the aqueous layer in the form of its violet-coloured iron compound. Twenty-five grams of the fruit juice are diluted with water to 50 c.c., acidified with a few drops of concentrated sulphuric acid, and shaken with 100 c.c. of light petroleum. Fifty c.c. of alcohol are then added, the mixture is again shaken, and allowed to separate. Ten c.c. of the light petroleum layer are now transferred to a tube, mixed with 10 c.c. of a 0.1% ferric chloride solution, and the coloration obtained is compared with that produced by known quantities of salicylic acid. These comparison solutions are prepared by shaking 50 c.c. of a 0.1% salicylic acid solution with a few drops of sulphuric acid, 100 c.c. of light petroleum, and 50 c.c. of alcohol; quantities of 0.5, 1.0, 1.5, 2.0, etc., c.c. of the light petroleum layer are then transferred to separate tubes and mixed with 10 c.c. of the ferric chloride solution. The method may also be applied to the estimation of salicylic acid in jams, beer, and wine, but any alcohol present in the substances must be removed previously by evaporation in the presence of an alkali. The process described by Vierhout (Abstr., 1911, ii, 775) was found to be untrustworthy.

W. P. S.

A Colour Reaction of Gallic Acid and of Tannin (Tannic Acid) and its Application. O. SCHNEKKE (*Biochem. Zeitsch.*, 1913, 52, 271—274).—When 3 c.c. of a 1% solution of iodine in potassium iodide are mixed with 2 c.c. of a 1% solution of gallic or tannic acids, and the mixture is diluted to 300—500 c.c. with tap-water, a reddish-violet colour is produced. This is due to the alkaline constituents of the water, and the same colour is produced when dilute solutions of carbonates of alkali metals or other alkaline reacting salts and alkali salts of organic acids are substi-

tuted for tap-water. The reaction can be applied to the detection of gallic acid in plant materials and in pharmaceutical preparations, and also to the detection of alkalis. With more concentrated alkali carbonate solutions, or with alkali hydroxides, the colour is dirty brown.

S. B. S.

An Examination of the Kumagawa-Suto Fat Estimation Method, as Regards the Oxidation of the Fatty Acids and Unsaponifiable Substances during the Process. MUNEMICHI TAMURA (*Biochem. Zeitsch.*, 1913, 151, 463—483).—No change in either the weight or iodine number of the fatty acids is caused in the saponification of animal tissues in the Kumagawa-Suto process. Neither is any change produced in the acids during the course of the evaporation of the petroleum, as the same results were obtained when the solvent was distilled off in the presence of oxygen, hydrogen, and carbon dioxide. In drying at 50° in air, there is an increase in weight and a diminution of the iodine number after prolonged heating. In one or two hours, the time required by the Kumagawa and Suto process, the change is, however, so small that any error due to this factor can be neglected. The unsaponifiable substances also undergo changes when heated in air at 50°, but here again the change is so small during the time required for drying in the Kumagawa-Suto process that it may be neglected. The modifications proposed by Mottram for this process are therefore necessary.

S. B. S.

The Action of Milk on Certain Reagents. FRED. BORDAS (*Eighth. Inter. Cong. App. Chem.*, 1912, 18, 69—72).—Since *p*-phenylenediamine in the presence of an oxidising agent yields a blue coloration when brought into contact with a calcium salt, the author argues that the peroxydase reaction of milk is due to the presence of calcium salts in milk. The fact that boiled milk does not give the reaction is due to coagulation caused by the heating; when heated milk is homogenised or shaken with pure silica, it regains its power of giving the peroxydase reaction.

W. P. S.

Reactions of Digitoxin. C. REICHARD (*Pharm. Zentr.-h.*, 1913, 54, 687—692).—A large number of tests are given, of which the following seem the most characteristic. Sulphuric acid does not dissolve digitoxin, and is in the cold apparently without action, but on warming darkening sets in. Glacial acetic acid is a good solvent. If a little digitoxin is triturated with some ammonium molybdate, or potassium dichromate, and a drop of water, no action takes place on evaporation, not even on again evaporating with glacial acetic acid. If now sulphuric acid is added a clear solution is gradually obtained, which does not change in the cold, but gives on warming intense colorations, an azure-blue in the case of the molybdate and a nickel-green in the case of the chromate. These colours gradually fade, but return on warming, and this may be shown over and over again.

Digitoxin may be distinguished from a number of similar substances by not liberating iodine from a mixture of sodium iodate and sulphuric acid. It is not coloured red by bromine water, as stated in the literature, unless it contains impurities. If a drop of cobalt nitrate solution is evaporated and the residue mixed with a little digitoxin and then warmed with glacial acetic acid, the liquid on exposure to the air will turn yellowish-green. L. DE K.

Estimation of Tannin in Tea. HENRY L. SMITH (*Analyst*, 1913, 38, 312—316).—An application of Chapman's "cinchonine method" for the estimation of tannin in hops to the estimation of tannin in tea. Good results may be obtained when the caffeine is removed from the solution previously.

Ten grams of tea are boiled with 800 c.c. of water for half an hour, the liquid filtered hot, and the leaves washed with 200 c.c. of boiling water. When cold, the volume is made up exactly to 1000 c.c.; 50 c.c. of the liquid are then shaken four times in succession with 30 c.c. of chloroform, which completely removes the caffeine. After concentrating the liquid to one-half, 30 c.c. of saturated solution of cinchonine sulphate are added at once, and after a few hours the precipitate is collected on a Gooch filter, which is previously washed with a half-saturated solution of the reagent, dried, and weighed. After washing with a half-saturated solution of cinchonine sulphate, the precipitate is drained by suction, and, so as to prevent melting on warming, first dried over sulphuric acid in a vacuum desiccator and then dried at 100°. It may be taken to contain 55% of tannin.

L. DE K.

Estimation of Urea by Hypobromite. LÉON GRIMBERT and M. LAUDAT (*J. Pharm. Chim.*, 1913, [vii], 7, 569—574).—The authors, who use a nitrometer filled with mercury, noticed that on shaking the hypobromite solution a small but decided quantity of free oxygen is given off. This, however, is not due to any action on the part of the mercury.

In order to get correct results in the estimation of urea, by observing the volume of gas given off on adding hypobromite, it is necessary to conduct a blank experiment with a solution of pure urea of about the same strength. In both experiments the volume of gas should be corrected for temperature and pressure before comparing the results.

L. DE K.

Value of the Guaiacum Test for Blood-stains. HERBERT S. SREWSBURY (*Analyst*, 1913, 38, 186—189).—When properly carried out, the guaiacum test is of value in detecting the presence of blood in stains on linen, etc., but must, however, be regarded as a sorting test, and the indications it affords confirmed by supplementary tests. The guaiacum tincture employed must be prepared freshly, as when even only twenty-four hours old, it gives poor results. The fabric to be tested is moistened, and a few drops of guaiacum tincture are added; if no coloration is produced within a few seconds, a few drops of hydrogen peroxide solution (20 vols.) are

added. When blood only is present, a blue coloration develops within one second after the addition of the peroxide. Blood never reacts with guaiacum alone, but certain substances, such as oxydases, oxidising agents, etc., yield a coloration with the reagent before the peroxide is added. The presence of urine or sweat does not vitiate the test under the conditions given. The guaiacum test will readily reveal the presence of a blood-stain that has been washed thoroughly.

W. P. S.

Micro-chemical Estimation of Certain Blood Constituents.

IVAR BANG and K. O. LARSSON (*Biochem. Zeitsch.*, 1913, 51, 193—199).

—A description of the microchemical method for estimating total nitrogen and the nitrogen of extractives is given. The blood is taken upon filter paper, weighed on a micro-torsion balance, and the total nitrogen is estimated by Kjeldahl's method adapted for microchemical estimations, for which the apparatus is figured and described. The ammonia is collected in excess of standard hydrochloric acid, the excess being estimated after the distillation, by addition of potassium iodate and iodide, and titration of the iodine set free by $N/100$ -thiosulphate solution. For estimation of extractives the blood on the filter paper is coagulated in acid potassium chloride, the extractives removed, and the nitrogen estimated microchemically in the residue.

S. B. S.

The Employment of Neutral-red Paper for Estimation of the Alkali of Serum. J. SNAPPER (*Biochem. Zeitsch.*, 1913, 51, 88—90).—Attention is called to the advantages of using neutral-red paper instead of lacmoid paper when estimating the alkalinity of the serum by titration. Details as to the method of preparing this paper are given.

S. B. S.

Method of Analysis of Brain Lipoids. J. LORRAIN SMITH and WILLIAM MAIR (*J. Path. Bact.*, 1913, 17, 609—613).—A full account with certain modifications of the methods already described (A., 1911, ii, 1006).

W. D. H.

The Bacterial Testing of Disinfectants. CHARLES T. KINGZETT and REGINALD C. WOODCOCK (*Analyst*, 1913, 38, 190—197).—The authors have determined the Rideal-Walker coefficients of a large number of chemical substances, all of which are known to possess either oxidising, antiseptic, disinfectant, preservative, corrosive, or lethal properties, and the results obtained lead them to the conclusion that the Rideal-Walker test is untrustworthy for ascertaining the real disinfectant value of sanitary preparations. They are of opinion that the only gauge of utility of the various disinfectants is the extent to which, as shown by experience, they may be employed satisfactorily for the particular purposes for which they are intended.

W. P. S.

General and Physical Chemistry.

Refractive Power of Liquid Hydrogen. WALTHER MEISSNER (*Ber. Deut. physikal. Ges.*, 1913, 15, 540—554).—Liquid hydrogen was produced by means of a Nernst liquefaction apparatus, which is described in the paper. The refractive index was determined by Wiedemann's method. The following refraction quotients, between liquid hydrogen and the gas between the suspended parallel plates, are found: white light, 1.1087, $\lambda = 0.656\mu$, 1.1098, $\lambda = 0.589\mu$, 1.1096 and $\lambda = 0.491\mu$, 1.1101. The relationship between the refractions of liquid and gaseous hydrogen is considered, and the values of liquid hydrogen are calculated. The calculated values agree with the observed values within the limits of experimental error. Liquid hydrogen is shown to possess no dispersion of magnitude greater than the experimental error.

J. F. S.

Double Spectrum of Sodium Chloride. WILDER D. BANCROFT (*Eighth Inter. Cong. App. Chem.*, 1912, 20, 37—43).—The author considers the causes of the differently coloured luminescence of sodium salts under different conditions. It is shown that when sodium burns slowly in chlorine or oxygen a blue light is emitted; the same light is emitted when sodium chloride is fused, when sodium chloride is placed in the layer separating the oxidising and reducing zones of a Bunsen flame, when sodium chloride is precipitated by alcohol or hydrochloric acid, and when sodium chloride crystals are crushed. The light in all these cases is produced by the change from sodium ion to undissociated sodium chloride. Cathode rays excite the blue luminescence in sodium chloride, whilst canal rays excite a yellow luminescence. The blue luminescence in the Bunsen flame is found where the rate of oxidation of the reduced sodium is slowest, at the surface between the oxidising and reducing zones. The yellow luminescence is observed where the rate of oxidation is higher, that is, in the oxidising zone. The simplest assumption in regard to the reaction producing the yellow sodium flame is that it is due to the change from sodium to sodium ion. This assumption is inadequate because it does not take into account the other spectra of sodium observed by Lenard (*Ann. Physik*, 1903, [iv], 11, 636) and Wood (*Astrophys. Journ.*, 1911, 72). Under the influence of cathode rays potassium iodide emits green light. Part of this light is probably due to the iodine, and it seems possible that the chlorine may be responsible for some of the white light observed with many chlorides. Whilst it is probable that the crystalloluminescence and the triboluminescence of potassium iodide are the same as the cathodoluminescence of this salt, the experimental evidence is insufficient definitely to decide the question.

J. F. S.

Vapours and Band Absorption [Spectra]. F. BURGER and JOHANNES KOENIGSBERGER (*Physikal. Zeitsch.*, 1913, 14, 725—726. Compare this vol., ii, 85).—An answer to Stark (this vol., ii, 539). J. F. S.

Absorption Spectra in the Red and Near Infra-red. AUGUST H. PFUND (*Eighth Inter. Cong. App. Chem.*, 1912, 20, 279—287).—The author has examined the absorption in the region 0.55μ — 1.5μ of ruby glass, cobalt glass, and chromium glass, also aqueous solutions of soluble Prussian-blue, sodium chromate mixed with cyanin, naphthol-green, naphthol-green mixed with cyanin, neodymium nitrate and distilled water. Absorption curves are given for all the substances. J. F. S.

Visible and Ultra-violet [Absorption] Spectra of Orange and Yellow Dyes Authorised for Use in Confectionery. GUSTAVE MASSOL and A. FAUCON (*Bull. Soc. chim.*, 1913, [iv], 13, 700—704. Compare this vol., ii, 264, 542).—Solutions of orange I, chrysoine, naphthol-yellow S, and auramine O in solutions of the concentration 1:10,000 were examined by the method previously described. Orange I allows all visible light up to the D-line to pass through; chrysoine allows a small amount of the green to pass; naphthol-yellow S rather more of the green; and auramine O transmits the whole of the green. In the invisible spectrum, chrysoine has no absorption bands. Orange I and naphthol-yellow S have each one band in the ultra-violet; the latter about $\lambda=285$, the former about 260. Auramine O has three bands in the ultra-violet at $\lambda=350$, 310, and 265. J. F. S.

Absorption of Ultra-violet Rays by Some Organic Colouring Matters in Aqueous Solution. GUSTAVE MASSOL and A. FAUCON (*Compt. rend.*, 1913, 157, 206—209).—The authors have studied the absorption of ultra-violet rays by aqueous solutions of the twenty-one colouring matters authorised for use in confectionery. These colours divide into two groups:

1. Those which absorb only the radiations of short wave-length.
2. Those which absorb both radiations of short and long wave-length, whilst allowing the intermediate ones to pass.

The rays used were between λ 2200 and 4045.

Group 1 comprises three pinks, eight reds, one blue, and two violets; whilst group 2 contains one orange, three yellows, two greens, and one blue.

Some of the colours possess distinctive absorption bands, which are of use in characterising them. These are set out in detail.

W. G.

Valency Electrons, Colour and Fluorescence. HANS VON LIEBIG (*Zeitsch. Elektrochem.*, 1913, 19, 559—570).—Polemical against Stark (this vol., ii, 456). A long criticism of Stark's views with regard to the constitution of organic substances and their fluorescence. J. F. S.

Connexion between Fluorescence and Ionisation. JOHANNES STANK (*Ann. Physik*, 1913, [iv], 41, 728—738).—Polemical against Volmer (this vol., ii, 456) and Pauli (this vol., ii, 456). The author also considers theoretically the relationship between fluorescence and ionisation of benzene, naphthalene and anthracene vapours.

J. F. S.

Oxidation and Luminescence. BLANCHETIÈRE (*Compt. rend.*, 1913, 157, 118—121. Compare Ville and Derrien, this vol., ii, 654).—On oxidation by a mixture of hydrogen peroxide and sodium hypochlorite, certain glyoxaline derivatives, 2:4:5-triphenylglyoxaline (lophine), amarine, and hydrobenzamide, show marked luminescence. The examination, under similar conditions, of a large number of organic compounds, having no chemical relation with glyoxaline, has never given luminescence. Certain natural products, such as urine, infusion of tea, and extract of meat, and many other substances, exhibit marked luminescence, but the author is as yet unable definitely to fix on any organic complex the oxidation of which results in luminescence.

W. G.

A New Luminescence of Calcium Compounds in the Hydrogen Flame, particularly those containing Bismuth or Manganese, and a Method of Detecting Traces of These Metals. JULIUS DONAU (*Monatsh.*, 1913, 34, 949—955).—The author shows that when calcium compounds are drawn through a non-luminous hydrogen flame, a bluish-green luminescence is produced. This is not produced by all calcium compounds, but only by those which contain traces of manganese. When a trace of a bismuth salt was placed on a piece of chalk and drawn through a hydrogen flame, a brilliant blue luminescence was produced. It is shown that, by taking pure chalk or gypsum and placing a drop of a solution containing a bismuth or manganese compound and then heating this on the lower edge of a hydrogen flame, traces of these metals may be readily detected. The reaction can be obtained for one ten-millionth of a milligram of bismuth and a millionth of a milligram of manganese. The luminescence is not affected by the presence of other metals. Barium and strontium compounds show similar but much less marked reactions.

J. F. S.

Experiments on Crystalloluminescence. EARL F. FARNAU (*Eighth Inter. Cong. App. Chem.*, 1912, 20, 127—128).—The author has noted the colour of the light emitted when sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium bromide, and potassium iodide were respectively precipitated from solution by alcohol, subjected to cathode rays, and formed from their elements. It is shown that the colour of the light emitted in the chemical reaction is the same as that produced during precipitation and during exposure to cathode rays.

J. F. S.

The Walden Reaction. CECIL L. HORTON (*Chem. News*, 1913, 108, 37).—Of the various reagents which have been employed to

effect substitutions and replacements in the study of the Walden inversion, only phosphorus pentachloride exhibits a constant behaviour, its action always being accompanied by a change in the sign of the rotation. With all other reagents the direction of the action is apparently dependent on the number of free carboxyl groups present in the parent substance. When the number of free carboxyl groups is even, the influence on the sign of the rotation is the reverse of that if the number of free carboxyls is odd. Thus the action of thionyl chloride, sodium hydroxide, potassium hydroxide, sodium methoxide, and ammonia on an active monocarboxylic acid gives rise to an active product having the same sign as that of the parent substance, whereas, if the latter contains no free carboxyl group or an odd number of carboxyl groups, the product has the opposite sign. The action of silver oxide, water, nitrous acid, nitrosyl chloride, and nitrosyl bromide is the reverse of that of the reagents last mentioned. Of the twenty-six examples quoted, only one forms an exception to the above rule, namely, *d*- α -bromoisovaleric acid, which, under the influence of ammonia, gives rise to *l*-valine, whereas the *d*-isomeride would be expected.

F. B.

Action of Light on Water Vapour and Electrolytic Gas. IVAN I. ANDRÉEV (*Zeitsch. Elektrochem.*, 1913, 19, 551–552).—Polemical against Coehn and Grote (*A.*, 1912, ii, 1118). The author answers the criticism against his work (*A.*, 1912, ii, 112).

J. F. S.

Action of Ultra-violet Rays on Solutions of Hydrogen Peroxide. VICTOR HENRI and RENÉ WURMSER (*Compt. rend.*, 1913, 157, 126–128).—A study of the photochemical decomposition of hydrogen peroxide by monochromatic light from the ultra-violet portion of the spectrum. The results confirm those of Tian for total light (compare *A.*, 1911, ii, 35) that the reaction is unimolecular, and that the velocity of decomposition is proportional to the concentration. For each wave-length the velocity is proportional to the incident energy. It is further proportional to the absorbed energy, the factor being a constant for wave-lengths between λ 2800 and 2060, the photochemical susceptibility varying proportionately with the absorption. Einstein's law of photochemical equivalence does not apply to the decomposition of hydrogen peroxide. The energy which must be absorbed for the decomposition of one gram-molecule of hydrogen peroxide is practically equal to the energy given out by the decomposition of the same amount of hydrogen peroxide in the dark.

W. G.

Additive Reactions between Carbon Monoxide and Other Gases under the Influence of Ultra-violet Rays. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, 157, 129–131).—The aptitude of carbon monoxide to form additive products is shown by its behaviour towards certain gases under the influence of ultra-violet light. In the presence of nitric oxide, a

small proportion of the carbon monoxide is oxidised by the oxygen set free from the decomposition of the nitric oxide. With water the reaction is more complex, one part of the carbon monoxide combining directly with the water, yielding formic acid, whilst the rest combines with the hydrogen and oxygen, resulting from the dissociation of the water, to give formaldehyde and carbon dioxide respectively (compare A., 1910, ii, 564, 606). Of the halogens, chlorine combines with carbon monoxide, but bromine and iodine are without action even in the ultra-violet light. Whilst combining with ammonia, it is without action on hydrogen phosphide or arsenide, and it does not react with hydrogen sulphide or free sulphur.

W. G.

Influence of the Wave-length on the Velocity of a Photochemical Reaction. MARCEL BOLL (*Compt. rend.*, 1913, 157, 115—118. Compare this vol., ii, 265).—From a study of the photochemical hydrolysis of the hydrochloroplatinic acids, the author has deduced the following formula governing the reaction: $m = \psi e^{av} P_0 s t c (1 - e^{-xlc}) / x$, where m is the weight of substance destroyed in a given time t ; ψ is a constant for each substance considered being its "photochemical lability"; v is the frequency, and P_0 the power of the incident radiation; s is the surface area irradiated; c the concentration of the solution; l the thickness of the layer; and x the coefficient of absorption. The constant ψ depends on the temperature and the nature of the reaction.

W. G.

Wave-length and Velocity of Reaction. LUDWIK BRUNER (*Zeitsch. Elektrochem.*, 1913, 19, 555—558).—The author considers and criticises the work of Winther (this vol., ii, 458) and Plotnikov (A., 1911, ii, 4, 452), and draws the conclusion that up to the present there is no evidence that photochemical reactions are influenced by the wave-length of the acting light, but rather that every kind of absorbed light energy plays an equal part in the velocity of the change.

J. F. S.

A Simple Method of Counting α - and β -Rays. HANS GEIGER (*Ber. Deut. physikal. Ges.*, 1913, 15, 534—539).—An apparatus consisting of a brass cylindrical box of 2 cm. diameter, fitted with an ebonite cover through which a metal rod passes, is described for the purpose of counting the α - and β -particles emitted by a radioactive substance. The bottom of the box is perforated by a round hole, and the rod is sharpened to a fine point. The box is raised to a potential of 1200 volts, and the rod is connected to an electrometer. The radioactive substance is placed at a short distance from the hole, the entrance of α - or β -particles into the chamber causes a passage of electricity to the electrometer, and from the amount of deflexion the number of particles can be calculated. By covering the opening by a piece of lead, the apparatus may also be used for counting γ -rays, although in this case the deflexion of the electrometer is due to secondary β -rays

(compare also Rutherford and Geiger (A., 1908, ii, 794; 1912, ii, 1021). J. F. S.

A Method of Determining the Number of Ions Produced by an α -Particle of Polonium. RENÉ GIRARD (*Le Radium*, 1913, 10, 195—198).—The method consists (1) in determining in absolute measure the saturation current I given by a film of polonium, supposed to be infinitely thin; (2) in counting the number of α -particles given in a known time in a small solid angle, and calculating N the total number given per second, supposing the emission is uniform in all directions. If e is the charge on an ion, and X the required number of ions produced per α -particle, $X = I/Ne$. The film of polonium was deposited from hydrochloric acid on a silver plate, which retained its brilliance and polish. The saturation current was measured by means of the quartz electric balance, and the α -particles were enumerated by means of a zinc sulphide screen in a vacuum. The mean value found for X was 116,000, the accuracy being estimated at 10%. This number is very much inferior to that found by Geiger (162,000) and by Taylor (164,000). The difference is ascribed to the fact that the ionisation current was measured for all the α -rays emitted over a hemisphere rather than for a narrow parallel pencil, and that some of the more oblique α -rays suffer appreciable absorption in the film of polonium. F. S.

Effect of Temperature on Cathodoluminescence. EARL F. FARNAU (*Eighth Inter. Cong. App. Chem.*, 1912, 20, 133—135).—Starting from the assumption that all forms of luminescence are due to chemical reaction, the author draws the conclusion that those conditions which increase the velocity of chemical reaction will increase the intensity of the luminescence. Cadmium sulphate and potassium bromide were placed in cathode tubes and cooled with liquid air, and as the salts cooled the luminescences decreased in intensity and finally vanished, the luminescence reappearing when the cooling agent was removed, thus confirming the author's initial assumption. J. F. S.

Radiation of Radium at the Temperature of Liquid Hydrogen. (Mme.) P. CURIE and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1430—1441, and *Le Radium*, 1913, 10, 181—186. Compare P. Curie, A., 1903, ii, 50, 255).—The ionisation produced by the γ -rays of radium at the temperature of liquid hydrogen, 20.3° Abs. has been compared with the ionisation at the ordinary temperature. The measurements were made in hydrogen. It is shown that no change of radiation occurs which has a greater value than 0.1%, and probably not even of 0.02%. Preliminary experiments were also made with polonium, and the same results indicated. J. F. S.

Radium Content of Some Alabama Coals. STEWART J. LLOYD and JOHN CUNNINGHAM (*Amer. Chem. J.*, 1913, 50, 47—51).—An examination of representative samples of various coals of Alabama

has shown that the amount of radium present ranges from 0.028×10^{-12} to 0.37×10^{-12} , with an average of 0.166×10^{-12} per gram of coal, or from 0.51×10^{-12} to 7.05×10^{-12} , with an average of 2.15×10^{-12} per gram of ash. The wide variation in the amount of radium per gram of ash is probably due to a specific tendency of certain plants to secrete exceptionally large quantities. E. G.

Colloidal Solutions of Radioactive Substances. FAIRZ PANETH (*Kolloid Zeitsch.*, 1913, 13, 1-4).—It is shown that the separation of radium-*E* and polonium from radioactive lead (Paneth, *Sitzungsber. K. Akad. Wiss. Wien*, 1912, 121, 2193) by dialysis is due to the fact that radium-*E* and polonium are both easily hydrolysed in aqueous solution. The basic salts or hydroxides thus formed remain in solution as colloids, and consequently do not pass through the membrane with lead and radium-*D*. If, on the other hand, a nitric acid solution of radioactive lead is dialysed, there is no separation. J. F. S.

Electric Conductivity of Thin Liquid Layers. A. UNGERER (*Physikal. Zeitsch.*, 1913, 14, 685-688).—The electro-conductivity of silver nitrate and sodium chloride solutions of varying concentrations has been compared with the conductivity of similar solutions in thin layers of the order 10^{-4} mm. The thin layers were obtained by pressing two plane glass plates together and regulating the thickness of the layer by means of the number and colour of the Newton rings visible. The conductivity was determined by means of a telephone arrangement, and also by direct current and a galvanometer. It is shown that conductivity ratio of the thin layer to the ordinary solution is independent of the concentration, that is, the conductivity of thin layers is relatively the same as that of solutions of ordinary dimensions. J. F. S.

Conductivity, Temperature-coefficients of Conductivity, Dissociation and Dissociation Constants of Certain Organic Acids between 0° and 65°. LESLIE D. SMITH and HARRY C. JONES (*Amer. Chem. J.*, 1913, 50, 1-46).—In continuation of earlier work on the conductivity and dissociation of organic acids (White and Jones, A., 1910, ii, 13, 821; Wightman and Jones, A., 1911, ii, 689; 1912, ii, 1035), a study has been made of a large number of acids, and the molecular conductivities, temperature-coefficients, limiting conductivities, percentage dissociation, and dissociation constants at various temperatures between 0° and 65° are recorded.

The results confirm most of the relations established previously. With regard to isomeric acids, it has been found that the ortho- and *cis*-forms are the stronger, that is, have the larger dissociation constants. It is also shown that the migration velocities of the anions are functions of the number of atoms they contain, and that most dibasic acids dissociate like monobasic acids. E. G.

Electric Conductivity of Salt Vapours. II. GERNHARD C. SCHMIDT (*Ann. Physik*, 1913, [iv], 41, 673-708. Compare A., 1911, ii, 788).—A continuation of previous work on the conductivity of

salt vapours. It is shown that the conductivity of the halogen salts of zinc and cadmium is independent of the time, when a concentration change is not brought about by the current and when the surface of the solid is kept constant. The fall in the conductivity, which is often observed as the measurements proceed, is due to a migration of the salt to the central electrode, with consequent change of concentration, and also to the change in the surface of the solid. The increase which is observed at the commencement of the measurements is due to the fact that the vapour only slowly reaches the electrode. The hypothesis previously stated by the author (*loc. cit.*) does not coincide with facts. With a constant surface, the concentration being kept constant, the conductivity first increases with increasing pressure, and then falls. The conductivity increases with increasing temperature.

J. F. S.

Liquid Helium. II. The Electrical Resistance of Pure Metals, etc. VII. The Potential Difference Necessary for the Electric Current Through Mercury Below 4.19°K . H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1406—1430).—The resistance of mercury at helium temperatures has been determined. It is shown that when a definite current strength known as the "threshold value" has been reached, the resistance practically disappears when the temperature 4.19°K is reached. The ratio of the value at 2.45°K to that at 273°K is expressed by 2×10^{-10} ohm. This represents the lowest value. It is shown that as the current strength is increased, the resistance rises due to heating effects occurring in the mercury thread itself, and not in any way due to conduction from the leads. The residual resistance of the mercury is evidently due to the mercury itself, and not to impurities, for mercury artificially amalgamated with traces of gold and cadmium lost its resistance at 4.19°K . Even mercury used for mirror preparation lost its resistance in the same way.

J. F. S.

Conductivity and Ionisation of Sodium Ethoxide, Potassium Ethoxide, Lithium Ethoxide, Sodium Phenoxide, Potassium Phenoxide, Lithium Phenoxide, Sodium Phenylthiourea, Sodium Iodide, Sodium Bromide, and of Mixtures of these Electrolytes in Absolute Ethyl Alcohol at 0° , 25° , and 35° . H. C. ROBERTSON and SOLOMON F. ACREE (*Eighth Inter. Cong. App. Chem.*, 1912, 26, 609).—The conductivities of these compounds in alcohol at 0° , 25° , and 35° have been determined in concentrations ranging from N to $N/256,000$. The percentage ionisation is much lower in concentrated alcoholic solutions than in the corresponding aqueous solutions, the ionisation of N -solutions of sodium ethoxide and sodium phenoxide, for example, being 14.8% and 12.2% respectively at 25° . The decrease in ionisation with rise of temperature is about 0.4—0.5% per degree. The maximum molecular conductivity is attained in concentrations between $N/2000$ and $N/8000$. The molecular conductivities of N , $N/2$, $N/4$, $N/8$, $N/16$, $N/32$, and

$N/8000$ solutions of sodium ethoxide at 25° are 4.93, 7.78, 10.37, 13.04, 15.98, 19.16, and 33.2 respectively.

E. G.

Electromotive Behaviour of Some Cadmium Elements. L. WILLIAM ÖHOLM (*Chem. Zentr.*, 1913, i, 1853; from *Acta Soc. Sci. Fennicae*, 1912, 41, No. 1).—The element $\text{Cd} \mid \text{CdCl}_2 \mid \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$ has an *E.M.F.* of 0.6717–0.6718 volt at 18° in saturated solutions. The variation with the temperature from 10° to 30° is given by the equation $E_t = 0.67179 - 0.000074(t - 18^{\circ}) - 0.0000015(t - 18^{\circ})^2$. The *E.M.F.* increases on dilution, reaching in $N/10\text{-CdCl}_2$ solution a value of 0.7447 volt at 18° . The temperature-coefficients of cells with dilute solutions are positive, and increase with the dilution. For the same current, elements with concentrated solutions are more polarised than elements with more dilute solutions. In the former, however, the depolarisation is much more rapid. The cells are constant in value, and not altered by shaking.

When cadmium bromide replaces the chloride, the *E.M.F.* falls to 0.5592 volt, and the temperature-coefficient becomes five times as great. The cadmium iodide cell has E_{18} 0.4147 volt. Cadmium sulphate cells have an *E.M.F.* of 1.0186 volts at 20° and the lowest temperature-coefficient of any cadmium cell.

There is very close agreement between the thermodynamical calculation of the heat liberation in these cells and the values determined calorimetrically. For cadmium chloride they are respectively 31,993 cal. (calculated), 31,984 cal. (found). E. F. A.

Gas-Electrode for General Use. GEORGE S. WALPOLE (*Biochem. J.*, 1913, 7, 410–428).—The apparatus and technique are described of an electrode for determining the hydrogen-ion concentration of protein solutions often containing dissolved carbon dioxide, within a few minutes and correct to 1 millivolt with 1 or 2 c.c. of fluid without loss or contamination. Sørensen titrations of 4% Witte peptone both colorimetrically and electrometrically are described.

E. F. A.

Mineral Electrodes. ROGER C. WELLS (*Eighth Inter. Cong. App. Chem.*, 1912, 21, 149–154).—Although it is known that pyrolusite, magnetite, and pyrite are conductors of electricity, it does not seem to have been recognised that some other sulphides are even better conductors than pyrite, and can therefore serve as electrodes. An account is now given of certain phenomena which have been observed when conducting minerals function as electrodes in aqueous solutions. The minerals studied, in the approximate order of their conductivity, are galena, pyrrhotite, magnetite, chalcocopyrite, and pyrite. Some of these develop potentials comparable with those shown by metals in contact with solutions of their salts. The potential is considerably affected by a change in the acidity or alkalinity of the solutions. Pyrite and marcasite are most positive in acid solutions; the potential falls as the solution becomes alkaline, and may even become negative in alkali sulphide solutions.

E. G.

The Product of an Electrolytically Disintegrated Carbon Anode, and the Existence of Colloidal Carbon. BARTOLO L. VANZETTI (*Kolloid. Zeitsch.*, 1913, 13, 6—9).—The author has prepared a quantity of the disintegration product by passing a current of 4 amps. per sq. dcm. through a dilute solution of sulphuric acid by means of carbon poles, which had been previously heated to 1000° in chlorine. On heating, the substance gives rise to water, carbon dioxide, and carbon monoxide. It is soluble in alkaline solutions, producing stable suspensions which are precipitated by acids. The colloid wanders to the negative electrode when electrolysed between platinum electrodes. The author discusses the evidence for and against the product being colloidal carbon or an organic substance of acid or phenolic nature. It is shown that there is not sufficient evidence to warrant a conclusion, but that there is no evidence which makes the idea of a colloidal solution of carbon impossible. J. F. S.

The Hall Effect in Liquid Electrolytes. A. E. OXLEY (*Proc. Roy. Soc.*, 1913, A, 88, 588—604).—The author has examined solutions of copper sulphate, silver nitrate, and cadmium sulphate, and a gelatin solution of copper sulphate under the influence of direct and reversed magnetic fields. The method adopted differs from that usually employed in the facts that the cells were very small in comparison with the pole pieces of the magnet, and a very sensitive Paschen galvanometer was employed. It is shown that in the experiments the effect observed is due largely to the Hall concentration effect, and that only a small portion is due to the true Hall effect. The potential differences in all the experiments are of the calculated order; they reverse with the magnetic field, and act in the same direction when the experimental conditions vary widely. The results are regarded as establishing the existence of a Hall effect in liquid electrolytes. J. F. S.

Co-precipitation of Copper and Carbon by Electrolysis: Oxidation at the Cathode. ELLWOOD B. SPEAR, C. CHOW, and A. L. CHESLEY (*Eighth Inter. Cong. App. Chem.*, 1912, 21, 93—97).—Lambris (A., 1910, ii, 131) has demonstrated the presence of carbon in the deposits obtained by the electrolysis of iron and nickel solutions, but has stated that, in the case of copper solutions, carbon is not precipitated under the same experimental conditions.

In the present paper, experiments are described which show that carbon is precipitated at the cathode during the electrolysis of a copper sulphate solution containing a little nitric acid and a small quantity of gelatin, and that some of the carbon is in the free state. It is considered that an oxidising action takes place at the cathode, and is doubtless due to secondary reactions. E. G.

Function of Inorganic Additive Agents in the Electrolytic Deposition of Copper. ELLWOOD B. SPEAR (*Eighth Inter. Cong. App. Chem.*, 1912, 21, 99—103).—In the electrolysis of copper solutions, the addition of certain inorganic substances under suit-

able conditions produces a beneficial effect on the deposition of the metal. The substances which have the greatest influence are nitric, hydrochloric, and sulphuric acids, and the nitrates and chlorides of ammonium and the alkali and alkali earth metals. It is suggested that the function of such agents is to keep the copper in solution. This theory is based on the assumptions that some particles of copper may assume the colloidal form at the moment of giving up their electric charges at the cathode, and that oxidation may take place on the cathode during the passage of the current. Experiments are described which show that copper is continuously dissolved and reprecipitated at the cathode during the electrolysis. The theory affords an explanation of the fact that good deposits of copper become loose and worthless if the electrolysis is continued too long.

E. G.

Present Theory of Magnetism and the Periodic System of Chemical Elements. JAKOB KUNZ (*Eighth. Inter. Cong. App. Chem.*, 1912, 22, 187—203).—A discussion of the electron theory of magnetism with special reference to Langevin's kinetic hypothesis of dia- and para-magnetism. It is shown that the phenomena are more complicated than Langevin's theory indicates, and that certain elements seem to exist in both the diamagnetic and paramagnetic state. A certain periodicity is pointed out between the atomic weights of the elements and their magnetic properties. A modification of the theory with regard to the difference between diamagnetic and paramagnetic properties is proposed. Ferromagnetism is discussed chiefly on the basis of Weiss's work, and particular attention is devoted to Weiss's magneton (A., 1911, ii, 183, 367, 694).

E. G.

Magnetic Researches. VIII. The Susceptibility of Gaseous Oxygen at Low Temperatures. H. KAMERLINGH ONNES and E. OOSTERHUIS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1404—1406).—The magnetic susceptibility of gaseous oxygen is determined between the temperatures of 17° and -126.7° at 100 times the normal density. It is shown that a Δ does not appear in oxygen above the critical temperature when the densities are 100 times the normal value. From this it appears probable that a Δ only appears for oxygen at great densities, and that in liquid oxygen it can rise to 71° as the density approaches 1000 times the normal value.

J. F. S.

Magnetic Investigation of Some Iron Compounds. W. HAGEN (*Kolloid Zeitsch.*, 1913, 13, 4—6).—The magnetic susceptibilities of a number of iron compounds have been determined, and the following relative values obtained: Ferric chloride, 1.000; ferric oxide, 0.116; iron formate, 0.784; iron acetate, 0.553; basic iron acetate, 0.540; iron valerate, 0.459; iron lactate, 0.810; iron malate, 0.675; iron tartrate, 0.634; iron citrate, 0.493; and iron saccharate, 1.010. Solutions of these compounds have been examined in the same way, and it is shown that they are mostly hydrolysed in solution, the

formate most strongly, and the citrate and malate only to the smallest extent. The formate and acetate contain all the iron in a colloidal condition in solution, and from the magnetic susceptibility it is shown that, in addition to colloidal hydroxide, another colloidal iron compound is present. The susceptibility of iron acetate and formate solutions increases with time, and eventually reaches a constant value, whilst the electric conductivity decreases to a constant value. On diluting ferric chloride with water, the hydrolysis increases with the dilution; sucrose solution and glycerol have the same effect, but dextrose and laevulose solutions decrease the hydrolysis.

J. F. S.

Decomposition of Complicated Chemical Compounds in a Variable Magnetic Field. ROMAN CEGIELSKIJ and, in part, E. I. LEDERER (*Ber. Deut. physikal. Ges.*, 1913, 15, 566—570).—Rosenthal (A., 1908, ii, 152) has shown that starch, sucrose, and certain proteins can be hydrolysed when a solution is placed in a continuously varying magnetic field. The authors have repeated these experiments, taking care to sterilise the solutions and containing vessels before the experiments. In no single case when the solutions were sterilised could hydrolysis be observed. In two cases, however, the solutions were not sterilised, and in these cases starch solutions were hydrolysed.

J. F. S.

The Heat Theorem of Nernst. HENDRIK A. LORENTZ (*Chem. Weekblad*, 1913, 10, 621—627).—A theoretical paper embodying applications of Nernst's theorem.

A. J. W.

Allotropy of Iron and Silver Iodide. CARL BENEDICKS (*Eighth Inter. Cong. App. Chem.*, 1912, 22, 13—27).—An allotropic change is not necessarily a sudden transformation of one modification into another, since there is always the possibility that one or both forms may have a certain solubility in the other, and in such cases the transformation in part takes place continuously.

Determinations of the dilatation of silver iodide from -180° to $+200^{\circ}$ have shown that the transformation point of this substance at about $+147^{\circ}$ affords an illustration of this fact. At low temperatures the dilatation is positive, but at 0° or the ordinary temperature it is negative. The dilatation must be ascribed to a solubility of the regular modification, stable above the transition point, in the hexagonal modification; this solubility increases with the temperature, and according to the curve of dilatation is probably very limited.

Consideration of the critical transformation point, A_3 , of iron at about 890° , and of the lower more undecided transformation range, A_2 , shows that the transformation at 890° is of the same type as that of silver iodide. According to this view, the so-called β -iron is really α -iron (stable at low temperatures), containing in solution a limited amount of γ -iron, increasing with the temperature (stable at temperatures above 890°). This conception greatly simplifies certain questions relating to the metallography of iron.

For example, the three most probable theories for the constitution of martensite when regarded from this point of view become identical.

E. G.

Contractive Volume- and Surface-Energy and Thermal Condition of Matter. PETR. P. VON WEIMARN (*Kolloid. Zeitsch.*, 1913, 13, 16—19).—A theoretical paper in which the author advances the view that the thermal condition of a substance is dependent on its dispersity. In considering the thermal condition of a solid substance, three surfaces have to be considered: (1) The outside surface, which bounds the substance from the surrounding objects; (2) the inner surface of contact of the crystalline particles; and (3) the inner pulsating surface of the crystalline particles.

J. F. S.

Thermal Properties of Carbonic Acid at Low Temperatures. C. FREWEN JENKIN and D. R. PYE (*Phil. Trans.*, 1913, A, 213, 67—117).—The thermal properties of carbon dioxide, liquid and gaseous, have been determined over the temperature range -50° to $+20^{\circ}$. The thermal quantities determined include: latent heat, total heat of the liquid, specific heat of the gas, dilation and elasticity of the liquid, and the Joule-Thomson effect for the liquid. From the experimental quantities, the specific volume and density of the saturated vapour and the specific heat of the liquid at constant pressure have been calculated. The pressure-temperature curve for the saturated vapour, and the entropy-temperature curve for the range $+20^{\circ}$ to -50° have been constructed. The following values of the specific heat of the gas have been obtained over the temperature ranges indicated, the former temperature being that at the commencement of the experiment, and the latter at the end of the experiment: -30.4° to $+7.8^{\circ}$, 0.22; -22.4° to $+8.6^{\circ}$, 0.25; -13.0° to $+11.2^{\circ}$, 0.275; -1.9° to $+9.1^{\circ}$, 0.32; $+8.3^{\circ}$ to 19.5° , 0.41; 14.9° to 25.6° , 0.435; 20.4° to 30.5° , 0.495; 24.6° to 35.4° , 0.55. The latent heat has a value 81.2 at -53.4° , which decreases to 36.56 at $+20.05^{\circ}$. The specific heat of the liquid at constant pressure has the value 0.47 at -50° , and 0.68 at $+20^{\circ}$. The value of the Joule-Thomson temperature change alters its sign at about -30° , being negative from 10° to -30° , and becoming positive at this point.

J. F. S.

Capacity for Heat of Metals at Different Temperatures. ERNEST H. GRIFFITHS and EZER GRIFFITHS (*Proc. Roy. Soc.*, 1913, A, 88, 549—560 *).—The authors have determined the specific heats of copper, aluminium, iron, zinc, silver, cadmium, tin, and lead at temperatures from 0° to 100° . The experiments were carried out with large quantities of the metals (1—3 kilos.), and the temperature differences never amounted to more than 1.4° . The temperature readings were made by means of platinum resistance thermometers. The specific heat of the metals examined at 0° bear the relationship to their atomic weights represented by $S=4.804 \times a^{-0.96}$, in which S represents the specific heat, and a the

* and *Phil. Trans.*, 1913, A, 213, 119—185.

atomic weight. By extrapolation the authors deduce that the atomic heat of the metals at absolute zero has a mean value of 4.813. J. F. S.

New Method of Measuring the Pressure of Corrosive Gases at Constant Volume. GEORGE S. FORBES and LESLIE BRIGGS COOMES (*Eighth Inter. Cong. App. Chem.*, 1912, 22, 79—85).—The determination of the pressure of corrosive gases at constant volume and high temperatures presents considerable difficulty, and the methods described hitherto are not satisfactory. Apparatus has therefore been devised which can be readily constructed. The pressure gauge is outside the oven, and is easily manipulated, and does not require calibration.

The apparatus consists of a glass bulb of about 250 c.c. capacity which has a small closed tube at the bottom and a tube at the top which carries a side-tube bent so as to emerge from the electric oven in which the bulb is heated. The tube, after leaving the oven, is bent horizontally and wound closely with fine nichrome ribbon to a point a little beyond the second of two depressions it bears. The first of these depressions is filled before the determination with a mixture of powdered fused lead and silver chlorides in molecular proportions. This mixture melts at about 350°. The tube is constricted at a point a little beyond the second depression, and the volume of the further portion is reduced by the introduction of a piece of glass rod. A piece of vacuum tubing connects the end of the tube with a section of thermometer tubing, and contains a smooth glass bead, which acts as an airtight seal unless the tubing is pinched at this point. By this means any rapid flow of air in either direction is prevented. At the end of the thermometer tubing where it is joined to the manometer is a fine capillary, which can be broken and re-sealed in order to admit air or to expel it from this part of the apparatus. The manometer is provided with a flexible tube, which enables the open arm to be raised or lowered at will to adjust the pressure.

If the pressure of the vapour of a liquid, such as phosphoryl chloride, or of a solid, such as iodine, is to be measured, a weighed quantity is sealed in a capsule of glass tubing provided with a very fine, closed capillary, and this capsule is inserted into the small closed tube at the bottom of the bulb. The bulb is then rendered nearly vacuum, and the upper end of the tube at the top of the bulb is sealed off. The mixed chlorides in the depression in the horizontal tube are fused by means of a small flame, and the tube is inclined by raising the bulb. The liquid flows towards the second depression, and forms a drop about 1 cm. long. A current just sufficient to keep it fused is passed through the nichrome ribbon. The drop readily responds to pressure changes of 0.1—0.2 mm. in the manometer, and thus enables the pressure in the bulb to be equated exactly to that in the manometer. The capsule is broken by means of gentle shaking at a temperature at which its vapour pressure does not exceed the pressure of the residual air in the bulb.

If a gas is to be investigated, it is admitted slowly into the vacuum bulb through a well-ground stopcock, and the drop is kept stationary in the tube by forcing in the requisite amount of air through the vacuum tubing.

The mode of calculating the results is explained, and experiments are described which demonstrate the practicability of the method.

E. G.

Vapour Pressure of Zinc Amalgams. JOEL H. HILDEBRAND (*Eighth Inter. Cong. App. Chem.*, 1912, 22, 147—156).—A study of the vapour pressure of amalgams has been undertaken with the object of testing the vapour pressure law on solutions differing widely in physical nature from the organic mixtures to which it has hitherto been applied, and also of investigating the general problem of metal compounds from a new point of view.

The results of some measurements of the vapour pressure of zinc amalgams are recorded. The values of the relative vapour pressures, P/P_0 , of the amalgam and, P_0 , of mercury are plotted against $N/N+1$, where N represents the number of mols. of mercury per mol. of zinc. If the amalgams were perfect solutions and obeyed the law $P/P_0 = N/N+1$, the curve should be a straight line, and the values $N/N+1$ and P/P_0 should agree. The results show, however, that the pressures are considerably higher than they should be for a simple solution. This divergence is explained by assuming that the solute is associated to some extent, and hence the number of mols. of zinc is less than is assumed in the simple formula. If the zinc was partly associated thus, $2Zn = Zn_2$, and α represents the number of mols. of Zn_2 formed from 1 mol. of Zn, there would remain $1-2\alpha$ mols. of Zn, and the total number of mols. present in the mixture would be $N+1-\alpha$. The values of $N/N+1-\alpha$, calculated from the law of mass action, agree closely with the observed values of P/P_0 , and thus indicate that the assumptions involved are correct. The extent of the association at various concentrations has been calculated, and it is shown that if zinc could exist in the liquid state at 300° , it would be associated to Zn_2 to an extent of two-thirds.

E. G.

Vapour Pressures of Some Concentrated Zinc Chloride Solutions. ALAN W. C. MENZIES and HENRIK BOVING (*Eighth Inter. Cong. App. Chem.*, 1912, 22, 219—220).—Determinations of the vapour pressures of zinc chloride solutions have given the following results, expressed in mm. of mercury at 0° : 60% solution, 4.4 at 14.64° , 8.1 at 24.64° , and 10.8 at 29.60° ; 65% solution, 2.5 at 14.64° , 5.0 at 24.64° , and 6.9 at 29.60° ; 79% solution, 1.4 at 14.64° , 2.9 at 24.64° , and 4.1 at 29.60° .

E. G.

The Rate of Evaporation of Liquids. PAUL DE HEEN (*J. Chim. phys.*, 1913, 11, 205—213. Compare Jablczynski and Przemycki, A., 1912, ii, 908).—In the author's measurements (1891) a stream of gas was allowed to impinge normally on the surface of a liquid, and the rate of evaporation was proportional to the product of the vapour tension and the internal friction of the gas. In Jablczynski

and Przemyski's recent experiments, the stream of gas was practically tangential to the surface of the liquid. Under these conditions a stationary saturated gaseous diffusion layer is formed, and the laws of evaporation are profoundly modified. Thus the relative rates of evaporation of water in hydrogen and in air are opposite in the two kinds of experiment.

Both normal and tangential gas streams were employed by the author in 1891, and Jablczynski and Przemyski's results are in better accord with the laws then established the more nearly their experimental conditions approximate to his.

R. J. C.

Thermal Analysis. FRANCESCO OLIVARI (*Chem. Zentr.*, 1913, i, 2001; from *Rendiconti Soc. Chim. Ital.*, 1911, 5).—Rudolfi (A., 1909, ii, 536) found no halt points in certain binary mixtures of organic compounds, and inferred partial isomorphism. Such points are now shown to exist in some of his cases. In the case of the system *m*-dinitrobenzene-naphthalene, an equimolecular compound exists which is strongly dissociated in the fused mass. A mathematical consideration is elaborated for the existence of compounds in the liquid phase which cannot be separated in the solid state.

E. F. A.

Heat of Formation of the Oxides and Sulphides of Iron, Zinc, and Cadmium. Heat of Combination of Acidic Oxides with Sodium Oxide. IX. WILLIAM G. MIXTER (*Amer. J. Sci.*, 1913, [iv], 36, 55–69. Compare A., 1912, ii, 899, and earlier abstracts).—The results of this work may be summarised as follows: $\text{Fe} + \text{O} = \text{FeO} + 64,300$ cal.; $2\text{Fe} + 3\text{O} = \text{Fe}_3\text{O}_3$ (faint red) $+ 192,200$ cal.; $3\text{Fe} + 4\text{O} = \text{Fe}_3\text{O}_4$ (magnetite) $+ 265,700$ cal.; $3\text{Fe} + 4\text{O} = \text{Fe}_3\text{O}_4$ (fused) $+ 265,200$ cal.; $2\text{FeO} + \text{O} = \text{Fe}_2\text{O}_3 + 63,700$ cal.; $2\text{Fe}_2\text{O}_3 + \text{O} = 3\text{Fe}_2\text{O}_3 + 54,500$ cal.; $\text{FeO} + \text{Fe}_2\text{O}_3 = \text{Fe}_3\text{O}_4$ (magnetite) $+ 9200$ cal.; $\text{Fe}_2\text{O}_3 + x\text{Na}_2\text{O} = \text{Fe}_2\text{O}_3 \cdot x\text{Na}_2\text{O} + 58,000$ cal.; $\text{Fe} + \text{S} = \text{FeS}$ (amorph.) $+ 18,800$ cal.; FeS (amorph.) $+ \text{S} = \text{FeS}_2$ (cryst.) $+ 16,700$ cal.; $\text{Zn} + \text{S}$ (rhombic) $= \text{ZnS}$ (cryst.) $+ 41,300$ cal.; $\text{CdO} + \text{Na}_2\text{O} = \text{Na}_2\text{CdO}_2 + 6500$ cal. (approx.); $\text{Cd} + \text{O} = \text{CdO}$ (amorph.) $+ 57,000$ cal.; $\text{Cd} + \text{O} = \text{CdO}$ (mostly cryst.) $+ 63,000$ cal.; $\text{Cd} + \text{S}$ (rhombic) $= \text{CdS}$ (cryst.) $+ 34,000$ cal.

Ferrous oxide can be obtained free from carbon or iron carbide by heating ferrous oxalate in a current of dry nitrogen. The temperature is gradually raised, until after four hours it is about 520° and carbon dioxide has ceased to be evolved. The temperature is then raised to 900° , and maintained at this point for an hour. The product thus obtained appears to be a mixture of FeO (4 mols.) and Fe (1 atom).

Reddish-brown, amorphous cadmium oxide volatilises or dissociates slowly at 900 – 1000° , but the rate of loss diminishes as the oxide becomes denser and crystalline.

E. G.

The Heats of Formation of Some Silicates of Iron and Manganese. S. WOLODZIN (*Compt. rend.*, 1913, 157, 121–123).—The author has determined the heats of formation of silicates of

iron and manganese, starting with pure quartz and ferrous oxide and manganous carbonate respectively. The figures he obtained for the molecular heats of formation are, for FeO, SiO_2 , 5905 cals., and for MnO, SiO_2 , 7725 cals., allowance being made in the latter case for the heat of dissociation of the manganous carbonate with formation of the oxide.

W. G.

Relation Between the Thermal Effect which Accompanies the Immersion of Dry, Powdered Substances in Liquid Substances and the Aptitude of the Latter to Form Associated Molecules. HENRY GAUDECHON (*Compt. rend.*, 1913, 157, 209—211).—The author has determined the amount of heat evolved per gram of dry powder on plunging a dried, powdered substance into a liquid without action on it. Four powders were used, and numerous liquids were examined. From the results the liquids arrange themselves in much the same order as from a study of the Pictet-Trouton coefficient LM/T , or the Ramsay-Shields coefficient K . The more abnormal the liquid with respect to these two laws, the more heat is evolved in the experiment. With normal liquids, the thermal effect is practically zero. From the results, it appears that the thermal effect depends principally (1) on the abnormal nature of the liquid; (2) on the area of the solid surface with respect to the weight of the solid, the greater part of the thermal effect being attributable to the aggregation or polymerisation of the molecules of the liquid at the surface of the solid.

W. G.

Characterisation of Flame. NICOLAE TECLU (*J. pr. Chem.*, 1913, [ii], 88, 189—192).—The author criticises the use of the term "flameless combustion" in connexion with the surface combustion of inflammable gaseous mixtures, and maintains that the combustion of the latter is invariably accompanied by the production of flame. The invisibility of the flame in the surface combustion of inflammable gas mixtures is due to the luminosity of the flame being very feeble in comparison with that of the heated surface at which the combustion occurs.

F. B.

Two Small Corrections to be Applied to Densities of Gases Determined at Geneva. PHILIPPE A. GUYE (*J. Chim. phys.*, 1913, 11, 319—326).—Recent measurements of gaseous densities at Geneva by the bulb method have shown a variation of less than 1 in 10,000. In reducing the weighings to vacuum standard at sea level in latitude 45° the normal weight of 1 c.c. of air has been assumed to be 0.00117 gram, and the gravity constant 980.616, and the platinum fractions have been corrected to vacuum standard independently of the brass gram weights. The first correction is not justified without taking into account the pressure, temperature, and humidity of the air at the time of weighing, and as the platinum fractions are standardised in air against brass, the whole of the weights should be considered as brass in applying vacuum corrections. The necessity for vacuum corrections is largely avoided

if the uncorrected tare of the bulb under similar meteorological conditions is known.

The most recent determinations of the gravity constant at Geneva, made in 1894 by Messerschmitt, gave $g=980.600$, corresponding with an error in the previous corrected values of $16/1,000,000$. A table is given of the total correction to be applied to various weights of gas on account of these considerations. The correction on 1 gram of gas, for instance, is 0.000068 gram, but there are other sources of error in bulb measurements which render these small corrections to some extent illusory.

R. J. C.

Specific Gravity and Displacement of Some Saline Solutions.

JOHN Y. BUCHANAN (*Trans. Roy. Soc. Edin.*, 1912, 49, 1-225).—An account is given of the determination of the specific gravity of solutions of the iodides, bromides, chlorides, nitrates, iodates, bromates, and chlorates of potassium, rubidium, and caesium at temperatures 15.0° , 19.5° , 23.0° , and 26.0° , the values being referred to water at the same temperatures as unit. Determinations were also made with solutions of sodium chloride, calcium chloride, magnesium chloride, and glucinum chloride. The concentrations of the solutions varied from solutions containing $1/1024$ of the gram-molecular weight in 1000 grams of water to those containing 9 gram-molecular weights in the same weight of water. In the case of the calcium chloride determinations, measurements were made with supersaturated solutions. All the determinations of solutions containing less than half molecular weight were made by specially prepared hydrometers, the more concentrated solutions were determined by means of a pycnometer, and for the supersaturated solutions the hydrometer was again used. A long description of the preparation of the hydrometer and its standardisation is given; this instrument resembles that used by the author on the *Challenger* Expedition. A description is also given of an open hydrometer for use with solutions of high specific gravity. The author considers the relationships between the displacement increments of analogous salts with change of concentration and the specific gravity of salts of nearly the same molecular weight, for example, RbCl , KBr , and $\text{K}(\text{Cl}+\text{I})/2$, which are generally found to be very much alike. The specific gravity of solid potassium chloride, bromide and iodide, rubidium chloride, bromide and iodide, caesium chloride, bromide and iodide, potassium chlorate, bromate and iodate, rubidium chlorate, bromate and iodate, and caesium chlorate, bromate and iodate are also determined. This is effected by weighing the crystals in their own saturated mother liquor at the saturation temperature in a specific gravity bottle. The following values, compared with water at the same temperature, are obtained at temperatures $24.3-22.8^{\circ}$: KCl , 1.951; KBr , 2.679; KI , 3.043; RbCl , 2.706; RbBr , 3.210; RbI , 3.428; CsCl , 3.982; CsBr , 4.455; CsI , 4.508; KClO_3 , 2.319; KBrO_3 , 3.219; KIO_3 , 3.924; RbClO_3 , 3.176; RbBrO_3 , 3.681; RbIO_3 , 4.336; CsClO_3 , 3.582; CsBrO_3 , 4.109; and CsI , 4.849. The specific gravities of the solutions are given to six places of decimals.

and it is shown that in many cases there is a probable error of only one or two units in the sixth place. Finally a series of factors is given for converting the values of ρ_{St} to ρ_{St} . In the determination of the specific gravity of supersaturated solutions of calcium chloride, the values fluctuated a great deal owing to rapid internal changes of temperature, from which it is deduced that the solution is internally in a state of unrest, which the author compares to the state of a gas or liquid at the critical temperature when under a pressure greater than the critical pressure.

J. F. S.

Viscosity of Gases at Low Temperatures. I. Hydrogen.

H. KAMERLINGH ONNES, C. DORSMAN, and SOPHUS WEBER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1386—1396).—The viscosity of hydrogen has been determined by the transpiration method from the temperature of solid carbon dioxide down to that of liquid hydrogen. The results are calculated on the basis of O. E. Meyer and Knudsen's formula. The results are recorded in a table along with those of Markowski and Kopsch (A., 1904, ii, 652). The value of $\eta \times 10^7$ is compared with the value calculated from Sutherland's formula, using the values $\eta_0 = 841 \cdot 10$ and $C = 83$. It is shown that there is a very great divergence at the lower temperatures between the observed and calculated values, which amounts to more than 100% at the temperature of liquid hydrogen. The authors deduce the formula $\eta = \eta_0 (T/273)^{0.685}$ to represent the relationship between viscosity and temperature. This formula is applied to the present results and to those of Markowski and Kopsch (*loc. cit.*), and gives good agreement over the whole range of temperature.

J. F. S.

Viscosity of Gases at Low Temperatures. II. Helium.

H. KAMERLINGH ONNES and SOPHUS WEBER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1396—1399. Compare preceding abstract).—The viscosity of helium is determined at temperatures from that of solid carbon dioxide to that of liquid helium by the transpiration method. The values of $\eta \times 10^7$ are given, and diverge widely from those calculated by the Sutherland formula. The relationship between viscosity and temperature is expressed by the formula $\eta/\eta_0 = (T/273 \cdot 1)^{0.647}$, which gives calculated values agreeing over the whole temperature range with the experimental values.

J. F. S.

Viscosity of Gases at Low Temperatures. III. Comparison

of the Results Obtained with the Law of Corresponding States. H. KAMERLINGH ONNES and SOPHUS WEBER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1399—1403. Compare preceding abstracts).—A theoretical paper, in which the dependence of viscosity on temperature is discussed. The viscosities of two mechanically similar systems are shown to give a constant ratio, which can be calculated from the expression $-\frac{1}{2} \log \eta / \sqrt{T \sqrt{M}} = \log \sigma - \log c$, in which M is the molecular weight, σ the mean radius of a molecule, and c a constant which is the same for all substances.

J. F. S.

Method of Measuring the Viscosities of Vapours of Volatile Liquids, with an Application to Bromine. ALEXANDER O. RANKINE (*Proc. Roy. Soc.*, 1913, **4**, 88, 575—588).—The author, making use of O. E. Meyer's transpiration formula, has devised a method of determining the viscosity of vapours of volatile liquids. The apparatus consists of two U-tubes of about 2 mm. internal diameter connected at one end to a capillary tube of 0.018 cm. diameter and 39 cm. long. One U-tube is filled with the liquid under examination, and the apparatus is exhausted and sealed. The U-tubes are placed in baths at known temperatures, one to evaporate the liquid, and the other to condense it. The capillary is placed in a third bath, which represents the experimental temperature. Experiments were carried out with bromine at temperatures from 13° to 220°, and the viscosity was determined; this quantity increases with temperature, and has the values in C.G.S. units at 12.9°, 1.511×10^{-4} ; 65.8°, 1.705×10^{-4} ; 99.8°, 1.885×10^{-4} ; 139.8°, 2.079×10^{-4} ; 179.8°, 2.273×10^{-4} ; and 220.4°, 2.480×10^{-4} . The author is able to calculate his values from Sutherland's equation, and with the exception of two values at the lowest temperatures, to obtain very good agreement. The values agree well with those obtained by the author by another method (*A.*, 1912, ii, 332).
J. F. S.

Determination of the Viscosity of Caoutchouc Solutions. PHILIP SCHIDROWITZ and H. A. GOLDSBROUGH (*Kolloid. Zeitsch.*, 1913, **13**, 46—48).—Polemical. The authors criticise changes made in their method of viscosity determination by Fol (this vol., ii, 301).
J. F. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. I. L. BERGZELLER (*Biochem. Zeitsch.*, 1913, **53**, 215—231).—The surface tensions of protein solutions which are sufficiently free from salts not to coagulate on heating, diminish strongly on boiling. On keeping, however, the surface tension increases again. The phenomenon can be explained on the assumption that a change in the size of the particles takes place. The surface tension of water is diminished by albumoses (Witte's or Grüber's peptone). These substances diminish the surface tension of a trypsin solution less than they do that of distilled water. The surface tension of a trypsin-albumose solution is not constant, but progressively increases on keeping, at first rapidly, then more slowly. The trypsin appears to form an unstable compound with the albumose, which is then hydrolysed. Pepsin acts in a manner similar to trypsin. During hydrolysis with trypsin and pepsin, the surface tension strongly diminishes, the amount of diminution running parallel with the amount of albumose formed.
S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. III. L. BERGZELLER and L. CSÁKI (*Biochem. Zeitsch.*, 1913, **53**, 238—255).—The authors confirm generally the results of Traube, who has shown that the addition of small quantities of

alkali to solutions of salts of alkaloids diminishes the surface tensions of the solutions, increasing at the same time the toxicities. With the aggregation of the alkaloid, in colloidal solution, which takes place on keeping, and more rapidly on warming than in the cold, the surface tensions again increase, whilst the toxicity diminishes. The alkaloids of the morphine series are an exception to this rule, as this is probably due to the chemical constitution of the substance, which has some relation to the surface-tension effects. A similar effect to the majority of alkaloids is observed when salicylic acid is separated from its salts by means of acids. This, again, is probably due to the existence of the free acid in colloidal solution. The adsorption of alkaloids by various adsorbents from alkaline solutions was also studied. By adsorption of the colloidal substance, the surface tension of the solutions was increased.

S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. II. L. BRÜTZLER (*Biochem. Zeitsch.*, 1913, 53, 232—237).—Pure caseinogen has no marked action on the surface tension of water. On boiling, however, the surface tension of water is diminished, and apparently a certain amount of hydrolysis takes place. If the caseinogen is dissolved in acids or alkalis, the surface tension of water is diminished considerably; the stronger the acid or alkali, the greater being the amount of diminution.

S. B. S.

Adsorption in Solutions, and the Chemical Processes Brought About Thereby. Adsorption in Aqueous Solutions of Potassium Dichromate and Potassium Chromate by Animal Charcoal. TADEUSZ ORYNO (*Kolloid. Zeitsch.*, 1913, 13, 9—14. Compare A., 1912, ii, 1145).—It is shown that potassium dichromate is strongly absorbed by animal charcoal, and that the absorption consists mainly in the absorption of $H_2Cr_2O_7$, which is probably converted into chromic hydroxide by reaction with the charcoal. It is found that after shaking for five minutes the $Cr_2O_7^{2-}$ concentration has decreased by 17.99%, and the K^+ concentration by 3.2%. The adsorption is much increased by the presence of 0.1N-hydrochloric acid, and in this process chromic ions are found in the solution. Sodium hydroxide retards the adsorption, and when the concentration 0.3N is reached entirely prevents it. This is attributed to the conversion of the dichromate into chromate, which, the author shows, is not adsorbed at all.

J. F. S.

Negative Adsorption. TADEUSZ ORYNO (*Kolloid. Zeitsch.*, 1913, 13, 14—16. Compare preceding abstract).—It is shown that on shaking potassium dichromate containing 0.3NaOH with purified animal charcoal, an increase in the concentration amounting to 6.5% occurs. This increase is independent of the time of shaking, and is uninfluenced by the addition of 1.2—0.15 molar sodium hydroxide, but more dilute solutions cause a positive adsorption. The amount of negative adsorption increased in proportion to the

amount of charcoal used. The change is explained by the assumption that there is an increased water concentration on the surface layer.

J. F. S.

Colloidal Constituents of Clay. PAUL ROHLAND (*Kolloid. Zeitsch.*, 1913, 13, 62—63).—The author advances evidence to show that the absorption of organic colouring matters is dependent on their structure. Those dyes derived from azo- or diazo-compounds are but slightly adsorbed by alumina. Thus it is shown that to absorb 0.003 gram of the following dyes, different quantities of alumina are required. Aniline-blue, victoria-blue, violet, and diamond-green require 5 grams; orange and vesuvine, 10 grams; and metanil-yellow, 30 grams. The yellow dye substance contained in the wash water of the sulphite cellulose manufacture is not absorbed at all.

J. F. S.

Kinetic Theory of Osmotic Pressure. GUSTAV JÄGER (*Ann. Physik.*, 1913, [iv], 41, 854—865).—The author has deduced from the analogy between a gaseous mixture of a compressed gas containing a small quantity of a second gas, and a solution, a kinetic theory of osmotic pressure, and from this developed mathematically the usual expressions for osmotic pressure and lowering of the freezing point of solutions.

J. F. S.

The Strenuous Period in the Development of the Theories of Solution. SVANTE ARRHENIUS (*Chem. Weekblad*, 1913, 10, 584—599).—An interesting autobiographical sketch, including an account of the evolution of the ionic theory, and of the criticism it evoked.

A. J. W.

Classification of the Colloids. RICHARD ZSIGMONDY (*Eighth Inter. Cong. App. Chem.*, 1912, 22, 263—274).—The various ways which have been proposed for classifying the colloids are reviewed, and a new scheme is put forward based on the behaviour of the colloid solutions on evaporation to dryness. The colloids are divided into (1) "resoluble" colloids, which, on evaporation of their solutions, yield a residue completely soluble in the dispersion medium, and (2) "irresoluble" colloids, which furnish a partly or completely insoluble residue owing to the occurrence of irreversible changes of state during the drying process. The first class is subdivided into (a) those which require the application of heat for the preparation of solutions, such as gelatin, starches, agar-agar, and many soaps, and (b) those which do not require to be heated, such as dextrin, gum arabic, Paal's colloidal metals, Graham's tungstic and molybdic acids, molybdenum-blue, and albumin. The irresoluble colloids are also of two kinds: (a) those which during drying yield pulverulent precipitates which are no longer peptisable, including pure metal colloids, certain sulphides, and salts, such as silver bromide and chloride, and (b) those which suffer an irreversible transformation on drying, and give peptisable jellies, such as stannic acid, silicic acid, and ferric oxide.

The classification of dispersed systems is also discussed. E. G.

Influence of Surface-active Substances on the Stability of Suspensoids. HUGO R. KRUYT (*Proc. R. Akad. Wetensch. Amsterdam*, 1913, 15, 1344—1349).—The influence of isoamyl alcohol, isobutyl alcohol, propyl alcohol, and ethyl alcohol on the limitation value of the absorption value of arsenic sulphide sols for barium chloride is investigated. The sol is shaken with the organic solvent, and then with sufficient barium chloride solution, so that the sol shall not be completely coagulated. The concentrations are found to increase with increasing concentration of the alcohol, that is, the limitation value is increased. The greatest increase is observed in the case of isoamyl alcohol, the others being, in decreasing order, isobutyl alcohol, propyl alcohol, and ethyl alcohol. This order is the same as that in which the substances reduce the surface tension of water. Some preliminary experiments with phenol are described which comes between isobutyl alcohol and propyl alcohol in its action.

J. F. S.

The Formula Expressing the Reduction in the Value of the Quantity b in the Equilibrium Equation with Diminution of Volume. JOHANNES D. VAN DER WAALS (*Chem. Weekblad*, 1913, 10, 628—634).—A theoretical paper.

A. J. W.

Equilibria in Ternary Systems. VI. FRANS A. H. SCHREINEMAKERS (*Proc. R. Akad. Wetensch. Amsterdam*, 1913, 15, 1298—1312).—A theoretical paper, in which the considerations of the previous papers are continued for the complex, solid-gas. The various transformations of the system are considered.

J. F. S.

Equilibria in Ternary Systems. VII. FRANS A. H. SCHREINEMAKERS (*Proc. R. Akad. Wetensch. Amsterdam*, 1913, 15, 1313—1326. See preceding abstract).—A theoretical paper, in which the behaviour of the systems containing two solid phases is considered under various changes of external conditions.

J. F. S.

Equilibria in Quaternary Systems. IX. Quaternary Systems with Ternary Mixed Crystals with a Gap of Miscibility. NICOLA PARRAVANO (*Gazzetta*, 1913, 43, i, 594—608. Compare this vol., ii, 571).—A mathematical discussion of this subject.

R. V. S.

Intramolecular Transformations. VI. Influence of the Solvent on the Equilibrium and the Velocity of Transformation. OTTO DIMROTH (*Annalen*, 1913, 399, 91—119).—The author has previously shown, by experiments on the methyl and ethyl esters of 5-amino-1-phenyl-1:2:3-triazole-4-carboxylic acid and their intramolecular transformation products, methyl and ethyl 5-anilino-1:2:3-triazole-4-carboxylates, that the displacement of the state of equilibrium, which a chemical system experiences through the influence of the solvent, is not dependent on any physical constant of the solvent, but is related to the solubilities of the reacting molecules. This relation is expressed by the

equation $c_A/c_B = Kl_A/l_B$, where c_A and c_B are the concentrations of the two modifications in the state of equilibrium, l_A and l_B are the solubilities, and K is a constant which is independent of the nature of the solvent

In order to verify this important relation and to widen the region of its applicability, two other pairs of structural isomerides have been examined, namely, methyl 5-hydroxy-1-methyl-1:2:3-triazole-4-carboxylate and methyl diazomalonomethylamide, and the ketonic and enolic modifications of benzoylcamphor. In the former pair of isomerides, in methyl alcohol, benzyl alcohol, acetone, ethyl acetate, ethyl nitrate, and nitrobenzene at 18°, although c_A/c_B (where A denotes the neutral isomeride, methyl diazomalonomethylamide) varies between 3.27 and 99 and l_A/l_B between 6.29 and 171.3, the value of K only varies between 0.52 and 0.68. This variation from constancy is attributed to the errors unavoidably introduced, partly by the enormously great solubility of the neutral isomeride as compared with that of the acidic form, partly by the fact that the value of c_A/c_B at 18° can only be obtained by extrapolation, the time required to attain equilibrium being thirty to forty days even at a temperature as high as 50°.

Similarly with the two forms of benzoylcamphor at 0° in ether, ethyl acetate, ethyl alcohol, methyl alcohol, and acetone, c_A/c_B (where A denotes the enolic modification) varies between 0.852 and 6.81, l_A/l_B between 0.748 and 6.39, and K between 1.06 and 1.15. The two varieties of benzoylcamphor are obtained by modifications of Forster's method (T., 1901., 79, 987); the ketonic form has m. p. 112° (Forster, 87—88°), and the enolic form, 90—91° (Forster, 89°).

Since $c_A/c_B > l_A/l_B$ at 0°, it follows that enolic modification of benzoylcamphor is stable in the crystalline state. This is verified experimentally by dilatometric method, whereby it is shown that the ketonic form changes to the enolic by long keeping. The transition temperature at which $c_A/c_B = l_A/l_B$, and therefore $K=1$, in other words, the temperature at which both forms can co-exist in the crystalline state, cannot be determined experimentally, but lies below -10°.

The author offers some interesting remarks concerning the relations between the solubilities and the constitutions of organic substances. These remarks can only be mainly speculations in the present state of our knowledge, but the author suggests that the solubility is a constitutive property in the sense that it is the product of factors each of which corresponds with each of the atomic groupings of which the molecule is composed. C. S.

System Oxalic Acid, Ammonium Oxalate, and Water at 30° and 45°. HERMAN W. WOUDESTRA (*Eighth Inter. Cong. App. Chem.*, 1912, 22, 251—257).—Three well-defined ammonium oxalates are known, namely, the normal oxalate, $C_2O_4(NH_4)_2 \cdot H_2O$, the hydrogen oxalate, $CO_2H \cdot CO_2 \cdot NH_4 \cdot H_2O$, and the tetroxalate, $C_2O_4H_2 \cdot CO_2H \cdot CO_2 \cdot NH_4 \cdot 2H_2O$. The equilibria have been studied which occur when mixtures of oxalic acid and ammonium oxalate

in different proportions are shaken with water at constant temperatures.

The isotherms of the system ammonium oxalate, oxalic acid, and water have been determined at 30° and 45°. The solubilities of oxalic acid at these temperatures are 12.59 and 21.015 grams respectively in 100 grams of solution, and those of normal ammonium oxalate are 5.53 and 8.3 grams respectively in 100 grams of solution. A saturated solution of normal ammonium oxalate deposits the tetroxalate both at 30° and at 45°. Graphical determinations of the solubility of the tetroxalate have shown that it is soluble to the extent of 7.21 grams in 100 grams of solution at 30°, and 11.12 grams at 45°.

E. G.

Applications of the Partition Law. WALTHER HERZ and W. RATHMANN (*Zeitsch. Elektrochem.*, 1913, 19, 552–555).—The partition coefficient of bromine, iodine, phenol, and acetone is determined between water and a number of aliphatic chlorinated hydrocarbons. From the results of the experiments at 25°, it is shown that bromine and iodine have normal molecular weights in tetrachloroethane, pentachloroethane, trichloroethylene, and tetrachloroethylene. Phenol is bimolecular in chloroform, tetrachloroethane, pentachloroethane, trichloroethylene, and tetrachloroethylene, and exists as bi- and ter-molecular complexes in carbon tetrachloride. Acetone is bimolecular in carbon tetrachloride and tetrachloroethylene, unimolecular in trichloroethylene, and forms complexes with chloroform pentachloroethane and tetrachloroethane.

J. F. S.

Gradual Hydrolysis. II. CARL L. WAGNER (*Monatsh.*, 1913, 34, 931–948. Compare this vol., ii, 200).—The author has examined dilute solutions of ferric chloride by means of an ultramicroscope, with and without the presence of potassium sulphate. It is shown that the gradual hydrolysis, as followed under the microscope, confirms the hypothesis put forward (*loc. cit.*) with regard to the gradual increase in the electric conductivity of ferric chloride solutions. The ratio between the surface of the colloidal particles at $t=0$ and $t=15$ is calculated, and this value agrees well with the corresponding ratio obtained from the electric conductivity. Similar experiments were carried out with zirconium nitrate, and the results obtained were found to be analogous to those obtained for ferric chloride.

J. F. S.

Studies in the Speed of Reduction. MORRIS LOEB (*Eighth Inter. Cong. App. Chem.*, 1912, 26, 601–604).—A study has been made of the effect of aluminium chloride on the behaviour of ferric chloride towards stannous chloride by a method similar to that employed by Noyes (A., 1895, ii, 257; 1897, ii, 17) in his investigation of the rate of reaction between ferric chloride and stannous chloride, and has shown that the rate of reaction between the two salts in $N/20$ -concentration is more than doubled when aluminium chloride is present in $N/20$ -concentration, whilst in presence of $N/10$ -aluminium chloride the rate is quadrupled. Manganous

chloride and glucinum chloride in $N/20$ -concentration also double the speed of the reaction, whilst a $N/20$ -quadrivalent thorium solution does not cause so great an acceleration.

When a solution of ceric sulphate is left under ordinary conditions, it gradually undergoes reduction to the cerous state. The rate of reduction is increased by dextrose, but the reaction does not follow a logarithmic law, the amount of cerium reduced being simply proportional to the time. When lanthanum sulphate or thorium sulphate is added to the ceric solutions, they exert an unmistakable influence on the rate of reduction by dextrose.

The variation in the velocity of these reactions seems to be due to a specific influence of the metals concerned, and probably indicates the formation of complex bases. E. G.

Contributions to the Chemical Kinetics of Enzymes. KIKUNAE IKEDA (*Eighth Inter. Cong. App. Chem.*, 1912, 22, 157—167).—The exact study of enzyme actions is rendered difficult owing to the gradual decay of the enzyme during the course of the experiments. Certain problems relating to the decay of the enzyme in the presence of the substratum are now discussed from a theoretical point of view. The case in which the velocity of the destruction of the enzyme is proportional to that of the transformation of the substratum is considered in detail, and certain deductions are made which are confirmed by Yamasaki's work on catalase.

The problem of the optimum temperature is also dealt with, and the relation between this temperature and the temperature-coefficient of the decay of the enzyme is elucidated. E. G.

Catalytic Studies. IV. H⁺-ion Catalysis and Autocatalysis of the Modified Hydrogen Peroxide-Thiosulphate Reaction. EMIL ABEL (*Monatsh.*, 1913, 34, 821—881. Compare this vol., ii, 399).—It is shown that the reaction between hydrogen peroxide and sodium thiosulphate in the presence of molybdic acid yields sulphate instead of tetrathionate according to the equation $4\text{H}_2\text{O}_2 + \text{S}_2\text{O}_3^{2-} \rightarrow 2\text{SO}_4^{2-} + 2\text{H}^+ + 3\text{H}_2\text{O}$. This reaction is accelerated by H⁺ ions in proportion to their concentration. The coefficient of acceleration is given by 3.5×10^7 at 25°, when the units are, time in minutes, and weights in gram-equivalents. The velocity of the sulphate formation is expressed by the equation $-d[\text{H}_2\text{O}_2]/dt = (1.5 \times 10^3 + 3.5 \times 10^7 [\text{H}^+]) [\text{MoO}_3] [\text{Na}_2\text{S}_2\text{O}_3]$. Since this reaction itself furnishes H⁺ ions, the change becomes autocatalytic. The velocity of the reaction in the presence of acetic acid and sodium acetate, added to define the H⁺-ion concentration, is given by the expression: $-d[\text{H}_2\text{O}_2]/dt = dy/dt = \{1.5 \times 10^3 + 3.5 \times 10^7 k((\text{CH}_3\text{CO}_2\text{H}) + y/4)^{1/2} \cdot a[(\text{CH}_3\text{CO}_2\text{Na}) - y/4]\} \cdot [\text{MoO}_3] \cdot (\text{Na}_2\text{S}_2\text{O}_3 - y/8)$, in which the quantities in round brackets represent initial concentrations, a the degree of dissociation of the acetate, and k the dissociation constant of the acetic acid. This equation admits of values being calculated which are in close agreement with the experimentally determined values. When the conditions of the

reaction are so chosen that the formation of both sulphate and tetrathionate occur simultaneously, the hydrogen-ion concentration is affected by both, the former producing hydrogen ions, and the latter removing them. The effect of the tetrathionate formation is consequently to retard the autocatalytic action of the hydrogen ion, and this can proceed so far as to convert a positive autocatalysis into a negative autocatalysis. With respect to the mechanism of the reaction, it is suggested that the catalysis is brought about by an oxidation, and that a highly dissociated permolybdic acid is produced as an intermediate product.

J. F. S.

The Intervention of the Number π in the Relationships between Atomic Weights. P. DAMBIER (*J. Chim. phys.*, 1913, 11, 260—266).—Two types of arithmetical relationship involving the number π exist between atomic weights. The first type, $R_1/R_2 = \pi/n$, where n is an integer, is exemplified in the ratio $3I/(Cl + Br + I) = 3.1417/2$, using Stas's atomic weights. The second type is $(M \pm n\pi)/(M' \pm n'\pi) = a/b$, where M and M' are molecular weights, and n, n', a, b simple integers. An example is $(HCl + 2\pi)/(NH_3 - 2\pi) = 4$, which leads to a value $\pi = 3.1416$ when the Geneva atomic weights are used instead of Stas's. It is urged that the intervention of π in these relationships is significant of some general connexion between the elements, but it must be assumed that atomic weights vary according as the atoms are neutral or ionised.

R. J. C.

The Intervention of the Number π in the Relationships Between Atomic Weights. PHILIPPE A. GUYE (*J. Chim. phys.*, 1913, 11, 267—268).—Such considerations as those put forward by Dambier (preceding abstract) and by Nicholson (A., 1912, ii, 35) must certainly be taken account of in the study of atomic relationships.

R. J. C.

Theory of Electrical and Chemical Atomic Forces. ALFRED BYK (*Ber. Deut. physikal. Ges.*, 1913, 15, 524—533).—A mathematical paper in which the author propounds a theory of the atom in which no structural hypotheses are contained. The applications of the theory to the physics and chemistry of the atom are indicated. The heat of dissociation of the chemical molecules and their cross section are calculated on the theory and compared with experimental results.

J. F. S.

Molecular Compounds as Primary Stages of Chemical Reactions. CARL ENGLER (*Eighth. Inter. Cong. App. Chem.*, 1912, 25, 131—140).—Evidence is adduced in support of the view that in many chemical reactions the reacting molecules first unite to form molecular compounds. Attention is directed particularly to the question of oxidation, and the author's theory expressed in his papers on autoxidation is emphasised, namely, that oxidation generally takes place by direct attachment of a molecule of oxygen

leading to the formation of a peroxide. This theory is confirmed by a series of investigations carried out by the author and his co-workers on the oxidation of organic compounds, such as the fulvenes and ketens. The course of the reaction in the formation of peroxides can be represented by the three following stages:

(1) $M:O:O$ (asymmetrical), (2) $M \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$ (symmetrical), and (3) $M \ll O$.

The asymmetrical oxide passes spontaneously, as a rule, into the symmetrical form, which is but rarely transformed into the stable modification (3). Hydrogen peroxide and ozone are quoted as examples of the first form, and barium peroxide and lead peroxide as examples of the second and third respectively. The second (and first) form corresponds with Schönbein's "autozonides" and the third form with his "ozonides."

E. G.

Electron Conception of Valence. III. Oxygen Compounds.

JOHN M. NELSON and K. GEORGE FALK (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 212—221. Compare A., 1911, ii, 104, 711).—The consideration of the direction of the valencies is extended to oxygen compounds. Owing to the pronounced electronegative character of oxygen, the problem is simpler than in the case of carbon, for in most cases the valencies can be assumed to be directed toward the oxygen atom, this having taken up two electrons, either from the same atom or two similar or different atoms. Tautomerism is due to the replacement of a hydrogen atom and the redistribution of the valencies of the other atoms, the oxygen atom always having two valencies directed towards it. The isomerism of the benzopinacolins should also be regarded as a case of tautomerism, the only difference being that a phenyl group migrates.

In the case of isomeric ketones, however, it is necessary to assume that the valencies in the carbonyl group are not both directed towards the oxygen atom. The symbol $C \equiv O$ is assigned to the more stable form, and $C \equiv O$ to the unstable.

The tautomeric forms of hydrogen peroxide are represented by the formulæ $H - O - O - H$ and $\begin{smallmatrix} H \\ \diagup \\ H \end{smallmatrix} O \equiv O$. The formulation of hydrates is exemplified with nickel chloride as type.

J. C. W.

The Conception of Valency as an Electronic Action. K. GEORGE FALK and JOHN M. NELSON (*J. pr. Chem.*, 1913, [ii], 88, 97—128).—The views expressed in this paper have already been published (A., 1911, ii, 104, 711, and preceding abstract). F. B.

Reminiscences of R. W. Bunsen. WILLEM A. VAN DORP (*Chem. Weekblad*, 1913, 10, 600—603).—An account of the author's personal experiences as a student in the Heidelberg laboratories under Bunsen in 1869.

A. J. W.

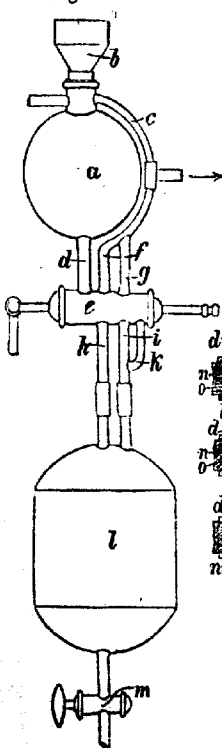
The Ring Figures in Frozen Gelatin. HUGO ROHONYI (*Biochem. Zeitsch.*, 1913, 52, 210—214).—If solutions of gelatin are poured into

a test-tube and then poured out again, and the thin layers of the solutions adhering to the glass are then frozen by the method described by the author, characteristic ring figures are formed, which are illustrated in the text. These are similar to Liesegang's figures obtained when silver nitrate is dropped into a film of potassium dichromate solution in gelatin. Ostwald's explanation of the Liesegang figures is quoted, and it is assumed that this also explains the phenomena with frozen gelatin recorded by the author.

S. B. S.

Combined Distillation Apparatus. LENHARD (*Zeitsch. angew. Chem.*, 1913, 26, 431).—A piece of apparatus is described which may be used for reflux and condensing operations. In the first case, the condenser is arranged vertically, and its lower end is attached to the flask by means of a short length of tube the ends of which form ground-in joints with the condenser tube and a tube sealed into the glass stopper of the flask; a tapped funnel is also sealed into the stopper. When required for distillation, the condenser is inclined and attached to the flask by means of a bent tube, the ends of which also form ground-in joints with the flask and condenser. W. P. S.

Fig 1



New Vacuum Filtering Apparatus for Continuous Filtration. WALTER DECKERT (*Zeitsch. anal. Chem.*, 1913, 52, 547—548).—The apparatus (see Fig. 1) consists of two reservoirs *a* and *l*, which are connected by means of a multiple-way stopcock *e*. On the reservoir *a* is placed the funnel *b*. The stopcock has three channels, of which two, *n* and *o*, run in an oblique direction parallel to each other (Figs. 2 and 3), whilst the third, *p*, terminates in an axial tube



Fig. 2



Fig. 3

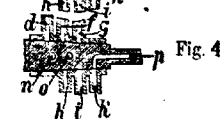


Fig. 4

giving communication with the outer air (Fig. 4). When the stopcock is placed in the position indicated in Fig. 2, the reservoir *l* is exhausted during the filtration in the passage *c g h l*; in the position in Fig. 3, the vacuum in reservoir *l* is obtained in the passage *c f i l*, whilst the filtrate runs through the passage *d h l* into the reservoir *l*. On placing the stopcock in the position indicated by Fig. 4, the outer air enters through the passage *p k l* into the lower reservoir, from which the liquid may then be run into a vessel by opening tap *m*. The bores in the stopcock are so arranged that in order to carry out the required manipulations, the stopcock has only to be turned like the hands of a clock; twice in succession 90°, once 180°.

The chief advantage of the apparatus is the withdrawal of filtrate without disturbing the filtering process. L. DE K.

Universal Extraction Apparatus. HAHN (*Chem. Zeit.*, 1913, 37, 880).—A modified form of apparatus serving for the extraction of solid matters as well as for heavy or light liquids, and requiring but little solvent. L. DE K.

Lecture Experiment. An Apparatus for the Volumetric Synthesis of Water. MILAN J. STRITAR (*Chem. Zeit.*, 1913, 37, 860).—The author describes a modified Hofmann apparatus for demonstrating the volumetric composition of water. It is claimed that the apparatus can be filled with mercury by one person without assistance, that it is easily obtained free from air, and that a comparatively small quantity of mercury (1.5 kilo.) is required to fill it. J. F. S.

Inorganic Chemistry.

Review of the Determinations of the Atomic Weight of Chlorine. The Atomic Weight of Silver. General Considerations on the Determination of Atomic Weights. PHILIPPE A. GUYE (*J. Chim. phys.*, 1913, 11, 275—318).—Since the international atomic weight of chlorine was fixed at 35.460, important determinations by Dixon and Edgar, Gray and Burt, Scheuer, Baume and Perrot, and Wourtsel have been described.

Recent determinations at Harvard of the atomic weight of chlorine by the two classic methods of Stas and Marignac lead to a value 35.454 when the atomic weight of silver lies between 107.87 and 107.88. Nine series of experiments by five different modern methods depending on gaseous interactions, such as the syntheses of nitrosyl chloride and ammonia, lead to a value $Cl = 35.461$ when $H = 1.00762$ and $N = 14.008$.

The difference between 35.454 and 35.461 corresponds with the presence of 0.02% of bromine in the chlorine, a quantity outside

the range of possibility. If the weight of an electron is 0.00054 atomic units, the difference between gaseous and combined chlorine might be as much as 0.003, but as this hypothesis cannot be verified, it is more profitable to regard the difference as due to experimental error. The modern methods are less circuitous than those based on the atomic weight of silver, and on account of the great variety of reactions used and the close agreement between different experimenters, the value 35.461 must be admitted to be correct. A slight impurity in the silver or the formation of a subchloride would vitiate the results obtained at Harvard.

If the atomic weight of chlorine is 35.461, the corresponding value for silver, namely, 107.89, must be considered possible. This value is arrived at directly from the ratio Ag:Cl (Richards and Wells), indirectly from the ratios Na:Cl (Smith) and Ag:NaCl (Richards and Wells), and also indirectly from the ratios Cl:Na, Na:Br, Br:Ag, and corresponds with any value for chlorine between 35.459 and 35.461. Further work is necessary to dispel the uncertainty as to the atomic weight of silver. A slight alteration in the accepted value for silver will lead to a wholesale revision of the values for phosphorus, the platinum metals, and many other elements.

The necessity for a concerted international scheme of atomic weight research is again urged.

R. J. C.

New Revision of the Atomic Weights of Chlorine and Nitrogen. EUGÈNE WOURTZEL (*J. Chim. Phys.*, 1913, 11, 214–248). Compare Boubnoff and Guye, A., 1911, ii, 599).—The experimental conditions necessary for a quantitative synthesis of nitrosyl chloride (A., 1912, ii, 934) are described. In Boubnoff and Guye's product an excess of chlorine was present because the temperature employed was below the solidifying point of the nitrosyl chloride, and some uncombined chlorine remained entrapped in the solid. In the author's experiments an excess of nitric oxide was used, and the reaction tube was shaken for fifteen minutes at room temperature under pressure to complete the reaction. No chlorine could remain uncombined, as nitrosyl chloride is stable up to $+700^{\circ}$, and any molecular compound, such as NOCl_2 , would be relatively unstable. When the nitrosyl chloride is solidified, the nitric oxide comes out of solution, and may be pumped off at -160° to -135° , the vapour pressure of nitrosyl chloride being practically zero at that temperature. The nitrosyl chloride was successively remelted, frozen, and exhausted three times to remove the last traces of nitric oxide before weighing. The mean atomic weight of chlorine was found to be 35.460.

Five determinations of the atomic weight of nitrogen were made by the synthesis of nitrogen peroxide from nitric oxide and oxygen. For convenience in weighing, the nitric oxide was dissolved in purified peroxide, but in less amount than that required for the complete conversion of the latter into trioxide. Excess of oxygen was passed in at -15° , and the excess removed by successively boiling the product at the temperature of solid carbon dioxide

and exhausting at -180° . The atomic weight of nitrogen was found to lie between 14.006 and 14.009, the mean value being 14.0075.

A method is described for the synthesis of pure nitrosyl chloride in quantity embodying the principles used by the author in his quantitative experiments. R. J. C.

Weight of a Normal Litre of Gaseous Chlorine and Silicon Tetrafluoride. Determination of the Atomic Weights of Chlorine and Fluorine. ADRIEN JAQUEROD and MELCON TOURPAIAN (*J. Chim. phys.*, 1913, 11, 269—274. Compare this vol., ii, 401).—Some unpublished determinations by Pellaton giving $+143.9^{\circ}$ and 79.6 atmospheres as the critical constants of chlorine are considered to be more trustworthy than the previous estimates by Ladenburg, Dewar, and Knietzsch, and are utilised in the calculation of the compressibility of chlorine by comparison with the data for sulphur dioxide and ammonia. The atomic weight of chlorine deduced from its density as determined by the authors is 35.296 with sulphur dioxide and 35.263 with ammonia as basis of comparison. The error in these values indicates that the physico-chemical methods are inapplicable to chlorine, or that gaseous chlorine is partly monatomic. The compressibility of silicon tetrafluoride directly adduced from Moissan's critical data or by comparison with the data for oxygen leads to a value 19.09 as the mean atomic weight of fluorine. It is suggested that the international atomic weight of fluorine, namely, 19.0, is too low. R. J. C.

The Spontaneous Transformation of Hypochlorites into Chlorates and of Hypobromites into Bromates. J. CLARENS (*Compt. rend.*, 1913, 157, 216—219).—The spontaneous transformation of hypochlorites into chlorates takes place through the intermediate formation of chlorites, but the latter cannot be detected, since in strongly alkaline media they disappear progressively without affecting the hypochlorite content. In old, commercial solutions of hypochlorites almost entirely converted into chlorates, chlorites are present in notable quantities.

The author has made a detailed study of this transformation in the case of hypobromites, which are converted into bromates, with the intermediate formation of bromites, and has determined the amounts of hypobromite and bromite present at different stages in the reaction. A theoretical discussion of his results shows that the bromate, the ultimate term in the evolution, is produced by the oxidation of the bromite existing in the liquid by the unchanged hypobromite. W. G.

Is the Proportion of Oxygen in Air Constant? OLIN F. TOWER (*J. Chim. phys.*, 1913, 11, 249—259).—According to Loomis (1875), a cold wave, accompanied by a high barometric pressure, corresponds with a low proportion of oxygen in the air which has descended from high altitudes, whereas Vogler (1882) suggested that a high barometer coinciding with a minimum of atmospheric

disturbance should lead to a concentration of oxygen at sea level. Jolly (1879) supposed that he had detected a diminished proportion of oxygen in wind blowing from equatorial regions where oxidation processes are rapid, and analyses by Hempel (1886) of air from Tromsø, Dresden, and Para seem to support this view.

More recent work by Durius and Zuntz (1894), Watson (T., 1911, 99, 1460), and Benedict (*Carnegie Inst. Report*, 166) indicate, however, that such small variations as occur in the proportion of oxygen are not traceable to meteorological conditions. The mean percentage of oxygen (20.952) found by Benedict from 1909 to 1912 corresponds very closely with the mean percentage (20.955) found by Morley in 1881.

R. J. C.

Reaction Between Ozone and Hydrogen Peroxide. VICTOR ROTHMUND (*Eighth Inter. Cong. App. Chem.*, 1912, 26, 611—615).—The estimation of ozone in presence of hydrogen peroxide can be effected iodometrically if potassium bromide is added to the weakly acid mixture before treating it with potassium iodide.

A study of the reaction between ozone and hydrogen peroxide in *N*/100-sulphuric acid solution has shown that when the peroxide is present in very large excess of the ozone (about 30:1), approximately equal numbers of mols. of the two substances are decomposed, but if more dilute peroxide is used, much more ozone is decomposed than peroxide. In alkaline solutions, however, the reaction takes place much more rapidly, and in the presence of excess of hydrogen peroxide, approximately equal numbers of mols. of the two substances suffer decomposition. These observations indicate that the reaction with the peroxide is accompanied by a spontaneous decomposition of the ozone, which is greatly accelerated by the presence of the peroxide.

E. G.

Sulphuric Acid and its Anhydride. HENRI GIRAN (*Compt. rend.*, 1913, 157, 221—223. Compare Pickering, T., 1890, 57, 338).—The author has confirmed Pickering's work on the solidification points of mixtures of sulphuric acid and water, and has completed his curve in the region between 68 and 76% H_2SO_4 , at which stage crystallisation is difficult to produce. The curve at this portion presents a maximum corresponding with the hydrate $H_2SO_4 \cdot 2H_2O$. To complete the curve, the author has studied mixtures of sulphuric acid and its anhydride, the curve showing only one maximum at 35° corresponding with pyrosulphuric acid. The last portion of the curve confirms the existence of the α - and β -modifications of sulphuric anhydride.

W. G.

Preparation of Telluric Acid and a Test for Associated Tellurous Acid. PHILIP E. BROWNING and H. D. MINNIE (*Amer. J. Sci.*, 1913, [iv], 36, 72—73).—The methods usually adopted for the preparation of telluric acid are not altogether satisfactory. Pure telluric acid can, however, be obtained by the following process. Powdered amorphous tellurium is suspended in water, and chlorine is passed into the mixture. About an hour after the tellurium

has dissolved, a portion of the solution is rendered alkaline, and afterwards acidified with acetic acid. If the solution remains clear, the tellurium has been oxidised completely to telluric acid. Experiments have shown that this test is capable of detecting 1 mg. of tellurous acid in presence of 0.1—0.2 gram of telluric acid in a volume of 5 c.c. When it is found that oxidation is complete, the solution is evaporated to a small volume, tested to ensure that reduction has not taken place, and again treated with chlorine if necessary. Acetone or alcohol is now added to the concentrated solution, and telluric acid is obtained as a crystalline precipitate.

E. G.

Constitution of [Carbon. OTTO DIMROTH and BERTHOLD KERKOVUS (*Annalen*, 1913, 399, 120—123).—By boiling wood charcoal with nitric acid, D 1.5, the authors have obtained, in addition to mellitic acid, a yellow, amorphous, very hygroscopic product, which has a strongly acid reaction, develops a black coloration with alkalis, dissolves easily in alcohol and ether, and by distillation of the barium salts, produced from it, with an excess of barium oxide yields benzene, naphthalene, and fluorene. Had fluorenone been obtained, there could be little doubt that this ring system was produced during the distillation. The production of fluorene itself, however, indicates that the yellow mass contains a carboxylic acid derived from fluorene, and, therefore, that the molecule of carbon contains C_5 -rings as well as benzene rings.

The research is being continued and extended to include graphitic acid.

C. S.

A Remarkable Condition for the Attack of Quartz by Gaseous Hydrogen Fluoride. ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1913, 157, 176—179. Compare A., 1912, ii, 806).—The attack of gaseous hydrogen fluoride on a polished surface of quartz is dependent on the inclination of the surface to the axis of the crystal from which it was cleaved. Quartz cut parallel to the axis and the facets at the point of a crystal corresponding with the inverse rhombohedron are moderately attacked, whilst a surface cut perpendicularly to the axis or the facets corresponding with the direct rhombohedron are hardly marked. The attack on a polished surface of previously melted quartz is much more vigorous, but even this is only about one-tenth of the action on glass.

W. G.

Density and Atomic Weight of Helium. WILHELM HEUSE (*Ber. Deut. physikal. Ges.*, 1913, 15, 518—523).—The atomic weight of helium has been determined from density determinations. The gas was purified by the usual method, and weighed against a glass counterpoise of about the same weight and volume as the vessel containing the gas. The weight of a normal litre of helium, as a mean of seven experiments, is found to be 0.17856 ± 0.00008 gram, from which the atomic weight is calculated as 4.002. J. F. S.

Nomenclature of the Complex Salts of Mineral Chemistry. GEORGES URBAIN (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 177—183).—Considerations are advanced which serve to justify the system of nomenclature of complex salts proposed by the French Commission of Nomenclature for Mineral Chemistry, in which carnallite, for example, is regarded as a double salt, $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$, and potassium platinocyanide as a perfect complex salt, $\text{K}_2[\text{Pt}(\text{CN})_4]$.
E. G.

The Solubility Scheme $\text{KCl} \cdot \text{MgCl}_2 \cdot \text{H}_2\text{O}$ (Carnallite Scheme), at 50° . JOHANNES UHLIG (*Centr. Min.*, 1913, 417—422).—A saturated solution in contact with solid potassium chloride and carnallite at 50° contains per 1000 mol. H_2O , 79.5 mol. MgCl_2 and 14.9 mol. KCl ; and when in contact with solid magnesium chloride hexahydrate and carnallite the solution contains 111.9 mol. MgCl_2 and 1.2 mol. KCl . Interpolating these values between van't Hoff's corresponding values for 25° and 83° , a slight error is noted in his values at 25° , for which a correction is made.

L. J. S.

The System Sodium Sulphate, Manganous Sulphate, and Water at 35° . FRANS A. H. SCHREINEMAKERS and D. J. VAN PROOIJE (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1326—1328).—It is shown that at equilibrium at 35° four solid phases are to be found: anhydrous sodium sulphate, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $9\text{MnSO}_4 \cdot 10\text{Na}_2\text{SO}_4$, and $\text{MnSO}_4 \cdot 3\text{Na}_2\text{SO}_4$. The authors are unable to detect the presence of the double salts, $\text{Na}_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, which have been previously described, whilst the double salts found have not been previously observed. It is thought that the two previously described salts are metastable under the conditions of the present experiments.
J. F. S.

Hardening of Gypsum. PAUL ROHLAND (*Kolloid. Zeitsch.*, 1913, 13, 61—62).—The author indicates that the hardening of burnt calcium sulphate with water is a colloidal process. The same applies to cadmium sulphate, copper sulphate, ferrous sulphate, and magnesium sulphate, which have been similarly treated. It is shown that only those sulphates harden, which in the crystallised condition contain several molecules of water of crystallisation. It is also pointed out that a strict division between crystal and colloidal water cannot be maintained.
J. F. S.

Borates. System $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ at 30° . III. UMBERTO SORCI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 798—801. Compare this vol., ii, 700).—In this paper the author discusses the results published in the two preceding papers on this system. The borates stable in contact with water at 30° are those containing the constituents in the proportions 1 : 1 : 6 and 2 : 3 : 9.
R. V. S.

Marls of Umbria. DANTE BACHILLI (*Gazzetta*, 1913, 43, i, 529—537).—The marls of Pontecentesimo (of which some analyses
51—2

are given) are suitable for the preparation of both rapid and slow setting cements, the properties of which have been investigated by the author.

R. V. S.

Action of Nitrogen on Strontium Carbide. SAMUEL A. TUCKER and Y. T. YANG (*Eighth Inter. Cong. App. Chem.*, 1912, 21, 121—126).—Tucker and Moody (A., 1911, ii, 883) have investigated the action of nitrogen on lithium carbide. A similar study has now been made with strontium carbide. The results of the experiments show that when strontium carbide is heated at 1000—1200° under atmospheric pressure, it absorbs nitrogen with formation of cyanide, cyanamide, and a little dicyanodiamide.

E. G.

Fusion of Carbonates under Carbon Dioxide Pressure. II. HENDRIK ENNO BOEKE (*Chem. Zentr.*, 1913, i, 1909—1910; from *Mit Naturforsch. Ges. Halle*, 3, 1—12. Compare A., 1912, ii, 760).—*The three modifications of Barium Carbonate.*—In addition to the reversible transformation of barium carbonate at 811° (compare A., 1906, ii, 753), there is a second transformation at 982°, accompanied by a very small heat change. The same transition point is observed on heating a polished plate of witherite. β -Barium carbonate is probably hexagonal, and α -barium carbonate regular in crystalline form. The presence of isomorphous calcium carbonate lowers the transition point at 811°. Neither the β - nor the α -form could be prepared at the ordinary temperature. The m. p. of barium carbonate is about 1740°. The following series of changes are established: $\gamma\text{-BaCO}_3$ (witherite, rhombic-pseudo-hexagonal) $\xrightleftharpoons[1740^\circ]{811^\circ}$

$\beta\text{-BaCO}_3$ (hexagonal) $\xrightleftharpoons[1632^\circ]{1740^\circ}$ $\alpha\text{-BaCO}_3$ (regular) $\xrightarrow{1740^\circ}$ melts.

System Barium Carbonate-Calcium Carbonate.—The experiments were made under a high pressure of carbon dioxide to prevent dissociation. The diagram corresponds with the formation of isodimorphous mixed crystals with a eutectic at 1139° containing 52.5 molecules % of calcium carbonate. There is no indication of the formation of a monoclinic compound, such as barytoalcite ($\text{BaCO}_3\cdot\text{CaCO}_3$). The conversions $\text{CaCO}_3 \rightleftharpoons \alpha\text{-CaCO}_3$ and $\beta\text{-BaCO}_3 \rightleftharpoons \alpha\text{-BaCO}_3$ were only very vaguely indicated. The conversion of $\beta\text{-BaCO}_3$ into witherite in presence of calcium carbonate was clearly evident to about 70% of barium carbonate, and showed a depression of 150°.

The molecular volumes of the fusions were determined pyrometrically in toluene, and plotted in a diagram. Those for mixtures containing 0—65% of barium carbonate lay on a straight line extending from the calcspar to the witherite points. Accordingly, the unstable rhombohedral barium carbonate has a molecular volume 46.3, $D=4.26$. The molecular volumes of mixtures with 25—30% of calcium carbonate lay on the line joining aragonite and witherite, that is, much lower; they correspond with the rhombic alstonite, which is only stable up to about 30 molecules % of calcium carbonate, and is then replaced by trigonal barytoalcite.

Strontium carbonate shows a transition point at 929° on heating, and 920° on cooling. α -Strontium carbonate is hexagonal. Pure strontium carbonate has m. p. 1497° .
E. F. A.

Corrosion of Lead by Calcium Hydroxide. WILHELM VAUBEL (*Zeitsch. angew. Chem.*, 1913, 26, 423—424. Compare A., 1912, ii, 1172; this vol., ii, 706).—The author shows that the corrosion of lead by calcium hydroxide is due to the presence of hydrated calcium peroxide in the hydroxide. The formation of the peroxide is attributed to the presence of iron. The reaction is expressed by the following equations: (a) $2\text{FeO} + \text{O}_2 = \text{Fe}_2\text{O}_4$; (b) $\text{Fe}_2\text{O}_4 + \text{Ca}(\text{OH})_2 = \text{Fe}_2\text{O}_3 + \text{CaO}(\text{OH})_2$; (c) $\text{CaO}(\text{OH})_2 + \text{Pb} = \text{PbO} + \text{Ca}(\text{OH})_2$. A further reaction is also supposed to take place, indicated by the equation: $\text{Pb} + \text{O}_2 + \text{Ca}(\text{OH})_2 = \text{PbO} + \text{CaO}(\text{OH})_2$.
J. F. S.

The Action of Water on the Carbides of the Rare Earths. A. DAMIENS (*Compt. rend.*, 1913, 157, 214—216. Compare this vol., ii, 700).—Varied results having been obtained by previous workers, the author has made a detailed study of the action of water on the carbides of the metals of the cerium group. The results show that in no case is methane produced, but that the principal gaseous products are members of the acetylene series, including acetylene, allylene, and higher homologues, together with small proportions of ethylene and ethane and their homologues. Some hydrogen is also obtained, and the production of ethylene and ethane probably arises from direct hydrogenation of the acetylene. In every case the metal was left in the form of its hydrated sesquioxide. The cerous hydroxide so obtained was white, and remained white even after desiccation out of contact of air. It rapidly absorbed oxygen to give ceric hydroxide.
W. G.

Baking of Clays. PAUL BRAESCO (*Compt. rend.*, 1913, 157, 123—125).—Clays, when mixed in the form of a paste, air-dried, and then subjected to heat, first dilate until a certain temperature is reached, when they cease to dilate, and begin to contract. The author has determined for a number of clays the temperatures at which contraction begins. Up to 1000° , mica, similarly treated, shows no sign of contraction, and when mixed with clays it raises the temperature at which contraction commences.
W. G.

Crystallisation of Steel. II. FEDERICO GIOLITTI and N. BOYER (*Atti R. Accad. Sci. Torino*, 1913, 48, 827—835. Compare *ibid.*, 609).—From the microscopic examination of steels tempered at various temperatures, the authors find that the production of a reticulate structure in hypoeutectic steels is not due to the crystallisation of ferrite at the periphery of the primary mixed crystals, but to the fact that the first crystals of ferrite formed act as "germs of crystallisation" for those subsequently produced as crystallisation proceeds.
R. V. S.

Influence of Intercrystalline Cohesion on the Mechanical Properties of Metals. JOHN C. W. HUMFREY (*Iron Steel Inst. Carnegie Mem.*, 1913, 5, 86—99. Compare Rosenhain and Ewen, this vol., ii, 119).—Microscopical observations are adduced to show that the intercrystalline junctions in iron and steel offer a great resistance to plastic deformation. When two neighbouring crystals have similar orientation, slipping along gliding-planes is readily transmitted. The crystals of metals are to be regarded as enclosed in a hard, continuous skin, highly elastic, but incapable of plastic deformation. The skin would appear to be of more than molecular thickness. The hypothesis is applied to explain the behaviour of overstrained metals. C. H. D.

A Thermometrically Recognisable Tempering of Quenched Steel at 100°. HERMANN SCHOTTKY (*Ferrum*, 1913, 10, 274—275).—When a sensitive thermometer is inserted into a hole drilled in a mass of hardened steel weighing about 50 grams, heated by means of a steam-bath, on approaching 100° the temperature of the steel rises suddenly, and then slowly falls. The effect is measured by making a parallel experiment with annealed steel, in which there is no such development of heat. The rise amounts to about 0·4°, and increases slightly with the temperature of quenching. It increases with the carbon content up to 1·22%, when the rise is 0·55°, and then falls. If interrupted before the development of heat is complete, and again heated, a second smaller rise of temperature is observed. A visible change of microscopic structure is not produced. C. H. D.

Specific Heat of Cold-worked Metals. C. CHAPPELL and MAX LEVIN (*Ferrum*, 1913, 10, 271—273).—Experiments have been made with steel containing respectively 0·07, 0·11 and 0·52% C, and with two tin bronzes containing about 6% of carbon. The materials are subjected to different degrees of cold working, and are also annealed in a vacuum. The specific heat is not found to vary more than the average experimental error, although on the whole the cold worked specimens have a slightly higher specific heat. The density of the cold-worked specimens is about 0·3% less than that of the annealed metals. C. H. D.

Specific Resistance and Hardness of Nickel-Cobalt Alloys. RUDOLF RUER and KIOSUKE KANEKO (*Ferrum*, 1913, 10, 257—260).—Cast alloys of nickel and cobalt, twice melted in porcelain tubes, are used, and are turned to 7·45 mm. diameter and 5 cm. long. The fall of potential with a current of from 25 to 50 amperes is measured in a paraffin-bath at 18°. The specific resistance of nickel rises rapidly with addition of cobalt, reaches a maximum at 20% Co, and then falls in a linear manner.

The hardness, determined by Brinell's ball test, is almost constant from 10 to 60% Co, rises sharply at 70% Co, and afterwards passes through a maximum at 90% Co. The discontinuity at 70% Co is also observed in the micrographic structure and the magnetic

properties (A., 1912, ii, 1059). Annealing at 1150° is necessary in order to equalise the hardness of the alloys in different portions.
C. H. D.

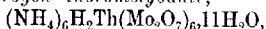
Autoxidation of Chromous Salts. JEAN PICCARD (*Ber.*, 1913, 46, 2477—2486).—Chromous salts on autoxidation in neutral or acid solution give rise to the formation of chromic acid as well as chromic salts. Intermediate products are formed having very marked oxidising powers, which, contrary to the usual opinion, are stable for a measurable period. These compounds can be titrated separately.

Oxide No. 1, $\text{Cr}(\text{OH})_2 \cdot \text{O} \cdot \text{O} \cdot \text{Cr}(\text{OH})_2$ (?), which is very easily decomposed, acts on potassium iodide in almost neutral solution. It decomposes rapidly into an extremely labile oxide, 1b, which, in the absence of potassium iodide, forms chromic acid, but which, in its presence, is reduced more rapidly than it can form chromic acid. The rate of decomposition into oxide 1b, $\text{Cr}(\text{OH})_2\text{O}$, is unimolecular.

Oxide No. 2, $\text{Cr}(\text{OH})_2 < \text{O}$, is reduced by potassium iodide in weak acid solution within two minutes. The formulæ ascribed to these oxides are purely hypothetical.
E. F. A.

Thoromolybdates. GIUSEPPE A. BARBIERI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 781—786).—Normal ammonium thoromolybdate, $(\text{NH}_4)_3\text{Th}(\text{Mo}_2\text{O}_7)_6 \cdot 8\text{H}_2\text{O}$, is obtained as a white precipitate when 10 grams of anhydrous thorium sulphate, dissolved in 200 c.c. of water, are added to 250 c.c. of a 30% solution of ammonium heptamolybdate. A solution of the thoromolybdate is almost completely precipitated by silver nitrate in presence of nitric acid, and the amount of silver nitrate required corresponds with 7.7 atoms Ag per molecule. The sodium salt, $\text{Na}_3\text{Th}(\text{Mo}_2\text{O}_7)_6 \cdot 15\text{H}_2\text{O}$, crystallises in needles and behaves similarly.

Ammonium hydrogen thoromolybdate,



is prepared by adding a concentrated solution of an ammonium salt to a nitric acid or hydrochloric acid solution of the above-described ammonium thoromolybdate. It is precipitated by silver nitrate. The corresponding sodium salt, $\text{Na}_6\text{H}_2\text{Th}(\text{Mo}_2\text{O}_7)_6 \cdot 17\text{H}_2\text{O}$, behaves similarly.

Silver thoromolybdate, $\text{Ag}_3\text{Th}(\text{Mo}_2\text{O}_7)_6$, is a white powder.

These salts do not give a precipitate with oxalic acid in the cold, but, on boiling, thorium oxalate is slowly deposited. The existence of these thoromolybdates is a point of similarity between thorium and the earlier members of group IV. The formulæ assigned to them (based on the views of Micolati [A., 1908, ii, 595]) are in good agreement with their properties.
R. V. S.

An Allotropic Modification of Bismuth. ERNST COHEN and A. L. TH. MOESVELD (*Chem. Weekblad*, 1913, 10, 656—658).—Bismuth exists in two enantiotropic modifications, the transition temperature being $75^{\circ}/760$ mm. The transformation of the form

stable below this temperature (α) into the other modification (β) is accompanied by considerable increase in volume. The β -variety can exist in the metastable condition below the transition point.
A. J. W.

Precipitation of Gold by Manganous Salts. A. D. BROKAW (*J. Ind. Eng. Chem.*, 1913, 5, 560—561).—When gold chloride solutions of varying concentrations are mixed with manganous chloride solutions (from $N/0.5$ to saturation), no reaction could be detected even after prolonged boiling. When, however, a very small amount of alkali is added to the cold mixture, manganese dioxide and gold are at once precipitated. The same result is obtained when a crystal of calcium carbonate is added to the mixture; there is a slight effervescence, and after a few hours the crystal is covered with manganese dioxide containing flakes of gold.

Amorphous manganous carbonate reacts at once with gold chloride with production of the dark brown hydrated dioxide. Crystallised manganous carbonate acts slowly, but after a day becomes coated with the dark brown hydrated oxide and flakes of gold.
N. H. J. M.

A Convenient Arrangement for Reduction with Colloidal Platinum or Palladium. OTTO STARK (*Ber.*, 1913, 46, 2335—2336).—In order to avoid the common danger of the introduction of mercury from the gas burette and the intrusion of air in experiments requiring the measurement of the absorbed volume of gas, the author uses, to contain the liquid for reduction, a glass holder provided with two taps and a tap funnel. At the commencement of an experiment, after the introduction of the solution to be reduced, hydrogen is passed through the vessel, passing on through the other tap and the attached india-rubber tubing to the empty gas burette, finally reaching the open atmosphere through the empty mercury reservoir. When all the air has been displaced, mercury is run into the reservoir and so into the graduated gas burette, whilst at the same time the tap by which the hydrogen entered is closed. The colloidal solution of platinum or palladium is subsequently introduced through the tap funnel, the mercury reservoir attached to the gas burette being lowered for the purpose.
D. F. T.

Osmium. ALEXANDER GUTHRIE (*Chem. Zeit.*, 1913, 37, 857—859).—

The author, in working up a quantity of osmium residues which contained quantities of organic substances, finds that the metal is not converted into the chloride when treated with chlorine, and in consequence the purification of the metal could not be effected in the usual way by means of the insoluble ammonium osmichloride. The following method has been evolved for the recovery of the metal from such residues. The dried residues are placed in porcelain boats in a hard glass tube, heated, and a current of oxygen is passed over; this burns away all carbonaceous matter, and the osmium is converted into the tetroxide, which distils over

into a series of U-tubes containing various reducing agents. As reducing agents, the author employs alcohol in slightly alkaline solution, ammoniacal alcohol containing ammonium chloride and an alcoholic solution of hydrazine hydrate. The reduced solution is evaporated to dryness on the water-bath, and then converted into the metal by heating in hydrogen and allowing to cool in carbon dioxide. The author shows that by this process it is possible to recover 2.83 grams of osmium from an artificially prepared mixture containing 3.0 grams of osmium.

J. F. S.

Mineralogical Chemistry.

Mineralogical-Chemical Investigation of Marcasite, Pyrites, and Magnetic Pyrites. ERICH ARBEITER (*Chem. Zentr.*, 1913, i, 1933—1934; from *Jahresber. Schles. Ges. Vaterländ. Kultur*, 1913. Compare Beutell, A., 1911, ii, 485, 728, 1094; 1912, ii, 652).—

Pyrites has the composition $(\text{FeS}_2)_2$, and the formula $\text{S} \begin{smallmatrix} \text{Fe} \cdot \text{S} \\ \text{Fe} \cdot \text{S} \end{smallmatrix} \text{S}$.

The constitution of the isomorphic cobalt-glance is accordingly

$\text{As} \begin{smallmatrix} \text{Co} \cdot \text{S} \\ \text{Co} \cdot \text{S} \end{smallmatrix} \text{As}$. That of marcasite is probably either $\text{Fe} \begin{smallmatrix} \text{S} \cdot \text{S} \\ \text{S} \cdot \text{S} \end{smallmatrix} \text{Fe}$

or $\text{S} \begin{smallmatrix} \text{Fe} \cdot \text{Fe} \\ \text{S} \cdot \text{S} \end{smallmatrix} \text{S}$. Marcasite is converted into pyrites between 400°

and 500°. Magnetic pyrites does not correspond with any definite chemical formula. That derived from meteorites approximately corresponds with FeS ; probably the excess of sulphur has been lost during the heating of the meteorite. Magnetic pyrites is regarded as a solid solution of FeS with a higher iron sulphide, probably one of low density. Lower sulphides are not present, and the supposition that dissolved sulphur is present is highly improbable.

E. F. A.

Chromite Segregations in the Platiniferous Dunites of the Urals. LOUIS DUPARC and SANTIAGO PIÑA DE RUBIES (*Bull. Soc. franc. Min.*, 1913, 36, 20—25. Compare this vol., ii, 714).—Irregular patches of granular chromite intermixed with some olivine occur in the dunites (olivine-rocks) of the Urals. The following analyses are of materials from different localities:

	TiO_2	SiO_2	Cr_2O_3	Al_2O_3	FeO	MgO	CaO	Total.
I.	0.24	0.82	55.60	9.68	23.20	12.26	0.34	100.14
II.	0.24	0.90	53.19	9.63	21.16	14.33	0.27	99.72
III.	0.40	0.82	52.67	10.56	23.37	12.23	0.24	100.29
IV.	—	1.83	35.88	8.57	42.61	10.04	—	98.93
V.	1.14	0.98	33.10	14.78	37.99	8.73	0.23	96.95

Deducting olivine, these analyses are re-calculated as follows:

	MgAl ₂ O ₄	MgCr ₂ O ₄	FeCr ₂ O ₄	FeFe ₂ O ₄
I.	13.82	36.95	38.95	12.12
II.	13.83	45.69	27.50	13.94
III.	15.12	32.66	41.57	11.44
IV.	12.62	21.25	31.09	37.64
V.	22.40	1.48	51.24	26.73

These analyses, taken in conjunction with those of the platinum ores from the same districts (A., 1911, ii, 733), suggest that chromite rich in the FeFe₂O₄ molecule is accompanied by platinum ores rich in osmium.

L. J. S.

Minerals from the Federated Malay States. (ANON.) (*Bull. Imp. Inst.*, 1913, 11, 243—248).—Several samples of tin-bearing sands and concentrates containing cassiterite, monazite, wolframite, ilmenite, etc., are briefly described, and partial analyses given. An analysis is also given of an impure manganese ore, containing MnO₂, 46.2; MnO, 11.45%.

L. J. S.

Minerals from the Pegmatites of Madagascar. LOUIS DUPARC, R. SABOT, and MAX WUNDER (*Bull. Soc. franç. Min.*, 1913, 36, 5—17).—The minerals described occur in pegmatite near Ambatofotsikely, north-west of Antsirabe. Fine large crystals of monazite have D 5.2735, and on analysis gave the results under I. Columbite is found as crystals of various habits and groupings, and also as large, crystalline masses weighing several kilograms; D 5.2726; analysis II. A radioactive mineral occurring in some abundance is referred (by reason of its composition, analysis III) to Lacroix's ampangabeite (A., 1912, ii, 567). It is resinous and reddish, but brownish-yellow on the exterior; D 3.3484 to 3.9236 in different specimens. The indistinct, rounded crystals are often intimately associated with columbite, and they are possibly pseudomorphous. The radioactivity of this mineral is about half that of pitchblende. The monazite and columbite are also slightly radioactive:

	SiO ₂	TiO ₂	ZrO ₂	ThO ₂	U ₂ O ₅	Cl ₂ O ₃	Ta ₂ O ₅	Ce ₂ O ₃
I.*	2.87	nil.	0.11	11.23	—	—	0.24	26.95
II.†	0.40	1.50	—	—	2.02	63.77	11.33	—
III.	1.75	2.10	—	1.30	12.50	50.60	—	5.75
	(La,Di) ₂ O ₃	(Y,Er) ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	MnO	CaO	Ign.	Total
I.*	32.60	0.30	0.15	0.60	nil.	trace	0.56	101.51
II.†	—	—	trace	—	8.79	—	—	99.61
III.§	2.10	1.35	1.20	7.20	1.53	1.83	11.55	101.06

* Also P₂O₅, 25.90.

† Also FeO, 11.38; SnO₂, 0.45.

§ Also SnO₂ + WO₃, 0.30; Cerium oxide as CeO₃, 5.75.

L. J. S.

Potassium-salt Deposits of Wittelsheim, Upper Elsass. ROLF VON GÖRGEY (*Tsch. Min. Mitt.*, 1912, [i.e., 1913], 31, 339—468).—A detailed description is given of the extensive deposits

of potassium salts recently discovered by boring in the Oligocene beds at depths of about 650 metres near Wittelsheim, north-west of Mühlhausen. Several analyses are given of mixed salts rich in sylvite, carnallite, etc., and of the associated anhydrite and dolomite rocks.

L. J. S.

Identity of the So-called Ihleite from Elba with Copiapite.

ERNESTO MANASSE (*Jahrb. Min.*, 1913, i, *Ref.* 386—388; from *Proc. verb. Soc. Toscana Sci. Nat.*, 1911, 20, 65—76).—A sulphur-yellow finely crystalline to powdery mineral, occurring together with other decomposition-products of pyrites and marcasite, has been described as ihleite by Görgey in 1907. A re-examination of this material proves its identity with the Chilean copiapite. The optical characters of the minute rhombic plates suggest orthorhombic, rather than monoclinic, symmetry. Analysis I of material from Vigneria, and II from Capo d'Arco. Deducting considerable amounts of admixed melanterite and alunogen, these analyses correspond with the copiapite formula, $\text{Fe}_4\text{S}_6\text{O}_{21} \cdot 16\text{H}_2\text{O}$. The impure, powdery mineral thus resembles the "misy" from the Harz:

	SO_3 .	Fe_2O_3 .	Al_2O_3 .	FeO .	MgO .	H_2O .	Insol.	Total.
I.	38.87	21.91	4.15	0.94	trace	33.33	0.61	99.81
II.	33.37	26.10	trace	4.06	—	30.63	0.71	99.92

L. J. S.

Cuspidine from the Inclusions in the Peperino of the Monti Albani. F. STELLA STARRABBA (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 871—875).—The cuspidine occurs in metamorphosed limestone near Ariccia, in the form of crystals having $D\ 2.95$, $a:b:c = 0.7243:1:1.9342$, $B\ 89^\circ 22'$.

R. V. S.

Epidesmine, a New Mineral. VOJTECH ROSICKÝ and STANISLAUS J. THUGUTT (*Centr. Min.*, 1913, 422—426).—This new mineral forms together with orthoclase a crystalline crust on large crystals of calcite from the Gelbe Birke mine at Schwarzenberg, in the Saxon Erzgebirge. The minute, water-clear crystals are orthorhombic with a prismatic habit. There are pinacoidal cleavages (100) and (010). $D\ 2.16$ and $n_{\text{xx}}\ 1.498$ are both very low. The acute negative bisectrix coincides with the vertical axis, and the optic axial plane is parallel to (100); $\gamma - a_{\text{xx}}\ 0.015$. The mineral is decomposed by dilute hydrochloric acid with separation of sandy-gelatinous silica. The following analysis gives, after deducting a small amount of admixed orthoclase, the formula $3(\text{Ca}, \text{Na}_2, \text{K}_2)\text{Al}_2\text{Si}_6\text{O}_{16} \cdot 20\text{H}_2\text{O}$, identical with that of stilbite. The microchemical colour reactions given by epidesmine are also the same as for stilbite:

SiO_2 .	Al_2O_3 .	CaO .	MgO .	K_2O .	Na_2O .	H_2O .	Insol.	Total.	D^{25} .
56.66	16.00	7.58	0.06	0.67	0.83	13.69	0.44	100.93	2.152

The orthorhombic epidesmine and the monoclinic stilbite (Germ. desmin) are thus dimorphous. A similar case of dimorphism

amongst the zeolites is afforded by epistilbite and heulandite (Germ. stilbit). These being alteration products of the feldspars, it is possible that their dimorphism bears some relation to the dimorphism of the latter (orthoclase-microcline and albite-barbierite).

L. J. S.

Montmorillonite from Bordes, Vienne, France. L. AZÉMA (*Bull. Soc. franç. Min.*, 1913, 36, 111—113).—The material forms a bed one metre in thickness in gravel, and consists of the following varieties: I, clear rose montmorillonite; II, greyish-white steatigillite; III, ochre-yellow common clay. These gave the following results on material dried at 100°:

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CoO, MnO, NiO	MgO	CaO	K ₂ O	Na ₂ O	H ₂ O	Total
I.	59.57	22.83	1.07	traces	3.82	2.21	—	—	10.46	99.96
II.	58.82	23.62	0.99	—	3.92	2.07	—	—	10.56	99.98
III.	59.00	18.62	11.39	—	1.04	1.04	2.38	0.13	6.45	100.05

Only fractional percentages of silica are soluble in alkalis. The formula is probably $H_2Al_2Si_4O_{12}, nH_2O$.

L. J. S.

Minerals [Chrysocolla] from the Belgian Congo. HENRI BUTTGENBACH (*Ann. Soc. géol. Belg., Publications relatives au Congo Belge*, 1913, 31—70).—Descriptions are given of a number of mineral species from this region. Chrysocolla occurs in the Étoile du Congo and several other mines in Katanga. It forms bright blue mamillated masses, interlaminated with malachite. Under the microscope, it shows a finely fibrous structure, with the fibres nearly perpendicular to the surfaces of crystallisation; the material is optically uniaxial and positive, and has a mean refractive index of 1.39. D 2.400—2.417. Analyses correspond with $CuSiO_3 \cdot 2H_2O$:

CuO	SiO ₂	H ₂ O	Insol. (CoO, CaO, Al ₂ O ₃)	Total
44.05	33.61	19.06	3.28	100.00
43.11	33.41	19.95	3.53	100.00

In a vacuum over sulphuric acid, the material loses 60.4% of its water, this being reabsorbed in a moist atmosphere; at 98°, 63.4%; at 255°, 85.4%; and it is completely dehydrated at 310°.

It has been suggested that chrysocolla is only a hydrated form of diopside ($CuSiO_3 \cdot H_2O$, which also is optically uniaxial and positive), or that it consists of diopside mixed with other substances. The two minerals are, however, shown to be quite distinct by their difference in density and refractive index, and by their behaviour when heated (diopside loses no water at 100°, and only 5% of the total water at 255°).

L. J. S.

The Matted-Fibrous Asbestos of Bohemia and Moravia. ALEX. E. FERSMANN (*Jahrb. Min.*, 1913, i, Ref. 381—382; from *Abh. böhm. Akad.*, 1912, No. 15).—In connexion with his work on palygorskite (A., 1908, ii, 603), the author has examined minerals of a similar nature from several localities in Bohemia and Moravia. These are referred to zillerite (tremolite- or actinolite-asbestos),

zermattite (serpentine-cork), β -palygorskite ($1A + 1B$, where $A = \text{parasepiolite, } H_4Mg_2Si_3O_{10}$, and $B = \text{paramontmorillonite, } H_6Al_2Si_4O_{14}, 2H_2O$), β -pilolite ($3A + 1B$), and parasepiolite. Analyses are given of the following: I, β -palygorskite from Dobešovic, Mies, Bohemia. II and III, ferruginous β -pilolite from Kuttenberg, Bohemia, occurring as a coating on calcite crystals in crevices in serpentine; IV, ditto from Pířibram; V, β -palygorskite from Obřan, Brünn, Moravia:

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	H ₂ O below 110°	H ₂ O above 110°	Total
I.	51.42	18.08	2.74	0.51	—	9.30	1.16	7.65	14.36	100.22
II.	56.04	trace	10.95	0.14	0.61	17.22	—	8.43	6.60	99.99
III.	54.68	1.83	9.67	0.67	trace	14.98	—	10.24	7.92	99.99
IV.	50.66	1.87	9.62	1.45	1.03	19.65	—	8.08	7.64	100.00
V.	54.17	13.56	0.22		—	9.55	0.41	9.58	11.87	99.36

L. J. S.

Dehydration of Micas. ALBERT BRUN (*Bull. Soc. franç. Min.*, 1913, **36**, 44—45).—The dehydration of powdered mica commences in a vacuum at 93° and proceeds regularly; at 360° one-quarter of the water is lost in the case of white micas, and four-ninths with black micas. Plates of mica are completely dehydrated when heated for half an hour at 830°, or for ten to twelve days at 510—540°. The material suffers no change in its optical properties, but, owing to the liberation of gas between the lamellæ, the plates become opaque (this can, however, be avoided by heating in a vacuum under certain conditions). All the micas when heated give off carbon dioxide, hydrocarbons, hydrogen, and nitrogen. The quantity of hydrogen liberated depends on the rate of heating, less being obtained when the material is heated very slowly. The water is regarded as existing in the micas in a state of solid solution.

L. J. S.

Spectrographic Study of Some French Mineral Waters. JACQUES BARDET (*Compt. rend.*, 1913, **157**, 224—226).—The author has examined spectrographically the dry residues from some fifty-four French mineral waters, with a view to furnish conclusive proof of the presence of some of the elements reported as present only in minute traces. In some cases he has proved the presence of metals not already noted, examples being gallium and germanium.

W. G.

Analytical Chemistry.

Application of Dialysis for Quantitative Estimations. A. GOLODETZ (*Zeitsch. physiol. Chem.*, 1913, **86**, 315—321).—A form of Soxhlet apparatus is described and figured, in which the liquid contained in a dialyser is placed in the Soxhlet tube surrounded

by distilled water, which passes into the receiver below, where it is boiled and condensed so as to flow back to the dialyser. In the case of easily decomposable substances the boiling can be done in a vacuum at a temperature of 40° . A concentrated solution of the material which dialyses is thus obtained in the receiver, and can be analysed.

E. F. A.

A New Indicator. FERENCZ ARON (*Chem. Zentr.*, 1913, ii, 381; from *Pharm. Post*, 1913, 46, 521—522).—Di-o-hydroxydistyryl ketone, $\text{CO}(\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$, is turned pale yellow by acids, and orange-red by alkali, the transformation being very sharp. The indicator is applicable for use with strong and weak acids and strong alkali, but not with ammonia. Three to four drops of a 1% solution suffice for 100 c.c. of liquid.

E. F. A.

Sodium Thiosulphate Solutions. CHARLES H. HAMPSHIRE and W. R. PRATT (*Pharm. J.*, 1913, 91, 142—143).—The strength of $N/2$ - and $N/10$ -sodium thiosulphate solutions remained unchanged when the solutions were kept for eight months under varying conditions as to exposure to light and the colour of the bottles in which they were stored. In certain cases small quantities of sulphur separated, but the decomposition was not of such a degree as to affect the titre of the solutions.

W. P. S.

Mercuric Oxide as a Standard for Volumetric Analysis. LEOPOLD ROSENTHALER and A. ABELMANN (*Pharm. J.*, 1913, 91, 144—145).—The use of pure mercuric oxide is recommended for standardising volumetric solutions of acids, alkalis, iodine, potassium permanganate, etc.

W. P. S.

Estimation of Chlorine in Natural Waters. JOSEF TILLMANS and O. HEUBLEIN (*Chem. Zeit.*, 1913, 37, 901—903).—The conclusions arrived at are as follows: The amount of potassium chromate added as indicator when titrating with silver nitrate is generally too small; 1 c.c. of a 10% solution should be added to 100 c.c. of the sample. Water containing less than 7.5 mg. of chlorine per litre should first be suitably concentrated. Waters containing a deposit of ferric hydroxide should be cleared by means of a little zinc oxide; dissolved manganese does not interfere. Acid effluents should be neutralised by means of a slight excess of magnesium oxide or sodium hydrogen carbonate; a blank titration experiment is recommended. Coloured waters may be bleached in acid solution by means of permanganate; the liquid is then neutralised as directed, and filtered. Amounts not exceeding 100 mg. per litre of peptone, phenol, soap, albumin, or urea do not interfere with the titration.

L. DE K.

New Form of Apparatus for the Estimation of Dissolved Oxygen in Water. GEORGE A. SOFER (*Eighth Inter. Cong. App. Chem.*, 1912, 26, 265—266).—The apparatus described permits of the addition of reagents to the water without exposing it to the air.

It consists of a bottle of about 500 c.c. capacity, with a long, funnel-shaped lip. A stopper, which is convex at the bottom, fits into the neck, and allows about 15 c.c. of liquid to stand in the funnel. The capacity of the bottle is determined with the stopper in its place. The estimation of dissolved oxygen is carried out in the following manner. The bottle is filled with the water up to the funnel, and the stopper is inserted. The excess of water in the funnel is poured off. The stopper is removed, and 6 c.c. of a standard solution, containing 48 grams of ferrous sulphate and 5 c.c. of concentrated sulphuric acid per litre, are delivered by a pipette to the bottom of the bottle. The stopper is replaced, and the water which rises in the funnel is poured off. Five c.c. of sodium carbonate solution (200 grams per litre) are then poured into the funnel, and the stopper is raised sufficiently to allow the solution to sink through the water to the bottom of the bottle. The stopper is re-inserted, the water in the funnel poured off, and the bottle is shaken until all the oxygen has been absorbed. Sulphuric acid (10 c.c. of a 50% solution) is now poured into the funnel, and the stopper raised sufficiently to permit it to diffuse through the liquid. The contents of the bottle are poured into a flask and titrated with a solution of potassium permanganate, each c.c. of which is equivalent to 1 c.c. of oxygen.

If the water contains much organic matter or sodium chloride, a blank experiment must be made, and the difference between the amount of permanganate required by the blank and that used in the actual analysis represents the quantity of dissolved oxygen present.

E. G.

Practical Field Method for the Estimation of Dissolved Oxygen in Water. GEORGE A. SOPER and PAYN B. PARSONS (*Eighth Inter. Cong. App. Chem.*, 1912, 26, 267—269. Compare Soper, preceding abstract).—The sample of water is collected in a separating funnel of 350 c.c. capacity after it has been filled and emptied several times by means of a special device described in the original. Solutions of ferrous sulphate and sodium carbonate are delivered by means of a pipette to the bottom of the funnel, which is then stoppered and shaken well. Sulphuric acid is now introduced through the stem of the funnel, the stopcock being opened for this purpose. The funnel is shaken and left for about five minutes, and the contents are then transferred to a flask and titrated with potassium permanganate. A blank experiment is now carried out by filling the separating funnel as before, adding sulphuric acid, shaking, and then adding the same volume of ferrous sulphate solution as in the previous experiment. The presence of the sulphuric acid prevents the dissolved oxygen from reacting with the ferrous salt. The funnel is shaken again, and the contents poured into a flask and titrated with the permanganate solution. The difference between the results of the two titrations gives the amount of ferrous salt oxidised by the dissolved oxygen.

E. G.

Estimation of Oxygen in Iron and Steel. JOSEPH A. PICKARD (*Iron Steel Inst. Carnegie Mem.*, 1913, 5, 70—85).—An improved hydrogen reduction method is described. The steel is placed in a nickel boat (previously ignited in hydrogen) contained in a silica tube closed at one end. This tube is provided with a glass extension carrying a T-piece. Hydrogen, generated from zinc and sulphuric acid containing ferrous sulphate, and purified by passing through potassium hydroxide, calcium chloride, and phosphoric oxide, is used for filling. About 20 grams of drillings are weighed and placed in the tube, a small unweighed boat containing phosphoric oxide being placed in the cool part of the tube, which is then exhausted. After a few minutes, hydrogen is admitted up to atmospheric pressure, the cap is removed, and a weighed boat containing phosphoric oxide is substituted for the other. The tube is washed out with hydrogen, and after admitting hydrogen up to one-half or two-thirds atmospheric pressure, an electric furnace, previously heated to 1000° , is slipped over the tube, and allowed to remain for forty-five minutes. After cooling, the boat is weighed. The correction for moisture introduced during the changing of boats is made by means of a blank, or by estimating the moisture in the air directly, the latter method being quicker. Carbon oxides and ferric oxide are completely reduced. Manganous oxide is not reduced when alone, but is apparently reduced when present in a steel. Slag is not reduced. C. H. D.

The Employment of Methyl-orange as Indicator for the Titration of Free Sulphuric Acid in Solutions of Copper Sulphate. ALFRED WOGRINZ (*Chem. Zeit.*, 1913, 37, 869).—Copper may be estimated in fresh copper-plating baths by titrating, in one sample, the total sulphuric acid after precipitation with hydrogen sulphide, and the free sulphuric acid in another portion. Methyl-orange may be employed for the latter purpose, sufficient being added to give such a reddish-violet colour that the colour of the copper ions is masked. At the neutral point the tint changes to light yellowish- or rush-green, but care must be taken to shake the liquid so that any precipitated copper hydroxide is redissolved. J. C. W.

Detection of Small Quantities of Selenious Acid. JUL. MEYER and J. JANNEK (*Zeitsch. anal. Chem.*, 1913, 52, 534—538).—To 1 c.c. of the solution containing selenium dioxide is added 0.1 gram of sodium hyposulphite ($\text{Na}_2\text{S}_2\text{O}_4$), and any free acid already present or formed by oxidation is neutralised with a few granules of sodium carbonate. The least traces of selenium present cause a red coloration due to colloidal selenium.

The reagent may be used for the detection of selenium in commercial sulphuric acid. In the absence of selenium, the precipitate consists of white colloidal sulphur, which is, however, yellow should selenium be present. Aqueous solutions, if too dilute for the test to show (limit 1 : 20,000), may be suitably concentrated; sulphuric acid, however, on concentration, loses its selenium content.

The Schultz petroleum test for the presence of selenium in sulphuric acid (formation of a dark brown colour) was found to be trustworthy.

L. DE K.

A Study of the Lassaigné Reaction. S. P. MULLIKEN and C. L. GABRIEL (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 208—211).—The authors perform the Lassaigné test by dropping the substance, in compressed pellets, into a red-hot iron test-tube containing 0.25 gram of sodium. It is often advantageous to make the pellets with naphthalene or sugar, and positive results have even been obtained by moistening pellets of naphthalene with a dilute solution of the substance. The amount of nitrogen fixed as cyanide was determined for several substances. Diazo-compounds give no cyanide.

J. C. W.

Estimation of Ammonia and Nitrogen. KNUBLAUCH (*Zeitsch. angew. Chem.*, 1913, 26, 425—431).—Convenient forms of apparatus are described for the estimation of ammonia and total nitrogen in such substances as spent oxide and other gas-works products. In the estimation of total nitrogen, the addition of mercury in the digestion with sulphuric acid must be omitted when the substances under examination contain thiocyanates, ferrocyanides, and double cyanides. It is recommended that, in this case, the substances should be treated with sulphuric acid, allowed to remain for five minutes, then heated gently for twenty minutes, and finally boiled for ten minutes. A quantity of 0.25 gram of mercury or 0.05 gram of cupric oxide is now added, and the mixture is boiled for one hour. The addition of mercury at this point does not matter, as the preliminary treatment with sulphuric acid decomposes the substances mentioned. In the subsequent distillation of the ammonia, the mercury ammonium compounds must be decomposed by the addition of a sulphide or of zinc dust, but in the latter case a definite excess of alkali must be present.

W. P. S.

Estimation of Ammonia and Trimethylamine. KOLOMAN BUDAI (*Zeitsch. physiol. Chem.*, 1913, 86, 107—121).—The aqueous solution of the hydrochlorides is mixed with an excess of formaldehyde (neutralised with 10 c.c. of phenolphthalein), and titrated, in presence of phenolphthalein, until a slight coloration is produced. The amount of ammonia is then calculated. The solution is now considerably diluted, made strongly acid with concentrated hydrochloric acid, and boiled down to one-third. When cold, it is transferred to a Kjeldahl flask, distilled with alkali into standard acid, and titrated as usual. The result gives the nitrogen as tertiary amine.

N. H. J. M.

Detection of Very Small Quantities of Nitric Acid in Waters. S. ROTHENFUSSEK (*Chem. Zeit.*, 1913, 37, 897).—One gram of diphenylamine is dissolved in 100 c.c. of pure (contact) sulphuric acid, of which 1 c.c. is then introduced into a stoppered glass cylinder. One drop of fuming hydrochloric acid is added, and

then pure sulphuric acid up to 100 c.c. After shaking, 20 c.c. of the mixture are placed in a beaker, and 10 c.c. of the sample of water to be tested for nitrates are rapidly added. On shaking, a blue colour appears, which increases in intensity. The reagent may be used for a ring test by placing 10 c.c. into a test-tube and pouring 5 c.c. of the water carefully over the surface. The coloration is very permanent.

L. DE K.

Estimation of Nitrates in Sea Water. WILLIAM R. COPELAND and GEORGE A. SOPER (*Eighth Inter. Cong. App. Chem.*, 1912, 26, 211—213).—A trustworthy method for the estimation of nitrates in sea water is of importance in connexion with the pollution of tidal harbours and the sea by sewage. It has been found that accurate results can be obtained by electrolytic reduction of the nitrates to ammonia by the copper-zinc method or the aluminium foil method, and subsequent estimation of the ammonia in the usual way. Various samples of land water, harbour water, and sea water have been tested, and nitrates were found to be present in every case.

E. G.

Quantitative Volatilisation and Separation of Phosphoric Acid from Metals of the Copper Group, and from Aluminium, Tin, and the Alkali Metals. PAUL JANNASCH and ROBERT LEISTE (*J. pr. Chem.*, 1913, [ii], 88, 129—167).—In continuation of previous work (A., 1909, ii, 759), the authors find that, when mixed with powdered quartz and heated to redness in a stream of carbon tetrachloride vapour, the phosphates of copper, silver, lead, cadmium, mercury, bismuth, potassium, and sodium may be completely decomposed and the phosphoric acid quantitatively volatilised.

The time required to effect complete decomposition is shortened, and the temperature at which the reaction proceeds lowered, if carbon dioxide and carbon tetrachloride are passed intermittently over the heated phosphates.

In the case of the phosphates of aluminium and tin, the addition of powdered quartz is insufficient to effect a quantitative separation of the phosphoric acid; complete volatilisation of the latter may, however, be accomplished if the phosphate is mixed with potassium chloride.

The paper contains a sketch and description of the apparatus employed in carrying out the decomposition by the intermittent method.

F. B.

Simple Method for Preparing Neutral Ammonium Citrate Solution. ANDREW J. PATTEN and W. C. MARTI (*J. Ind. Eng. Chem.*, 1913, 5, 567—568).—Fifty c.c. of a citrate solution are diluted to 250 c.c. Five c.c. of the diluted solution are treated with 4 c.c. of a neutral 40% formaldehyde solution, and titrated with $N/10$ sodium hydroxide, with phenolphthalein as indicator. The colour should remain when the solution is heated to boiling. The ammonia is estimated by distilling with magnesia. The difference

between the acid and ammonia titration gives the number of c.c. of $N/10$ -ammonia required to neutralise 1 c.c. of the acid citrate solution, from which the amount of a stronger solution of ammonium hydroxide required to neutralise any given amount of the acid solution may be calculated.

The method is accurate and easy; and it shows that the ratio of ammonia to anhydrous citric acid in the neutral solution should be 1 : 3.765, and that one litre of D 1.09 should contain $\text{NH}_3 = 44.76$ and $\text{C}_6\text{H}_8\text{O}_7 = 168.57$ grams.

N. H. J. M.

Estimation of Phosphoric Acid in Soils. RICHARD HORNBERGER (*Landw. Versuchs-Stat.*, 1913, 82, 299—302).—When hydrochloric acid extracts of soils containing titanium are precipitated with ammonium molybdate, more or less titanic acid separates, which remains undissolved when the molybdate is dissolved in ammonia. Owing to its fine state of division and partly colloidal state, some of the titanic acid passes through the filter, and afterwards forms flakes. When filtered and washed, it again passes through the filter. The separation of titanic acid cannot be overcome completely, and as the precipitate contains small amounts of phosphoric acid, a slight minus error is introduced when the precipitate is removed, and a plus error when it is not removed, before precipitating with magnesia mixture.

The error may be avoided by fusing the precipitate with sodium carbonate, extracting with water, and, after expelling the carbon dioxide, estimating the phosphoric acid by the molybdate method.

N. H. J. M.

Estimation of Hypophosphites, with Notes on Commercial Samples. T. TUSTING COCKING and JAMES D. KETTLE (*Pharm. J.*, 1913, 91, 132—134).—The use of potassium dichromate for the titration of hypophosphites is recommended. A quantity of 2.5 grams of the salt under examination is dissolved in water, an excess of a 10% lead acetate solution is added to precipitate phosphites, the mixture is diluted with water to 50 c.c., and set aside until the supernatant liquid is clear. Ten c.c. are then transferred to a flask, mixed with 50 c.c. of $N/1$ -potassium dichromate solution and 10 c.c. of sulphuric acid, and heated on a water-bath for one hour. After cooling, the excess of dichromate is titrated with thiosulphate solution after the addition of potassium iodide. The method may be applied to calcium, potassium, manganese, and iron hypophosphites, and results of analyses of these salts are recorded. In the case of hypophosphorous acid itself, it is necessary to neutralise the acid with sodium hydroxide before the addition of the lead acetate.

W. P. S.

Estimation of Hardness in Very Hard Waters. SANTIAGO PIÑA DE RUBIES (*Ann. Chim. anal.*, 1913, 18, 266—271; *Anal. Fis. Quím.*, 1913, 11, 98).—When determining the hardness in waters, the

sample has occasionally to be largely diluted, so that the experimental error becomes greatly multiplied.

Hence, in the absence of alkali carbonates, the author recommends the acidimetric method of Hehner or that of Wartha-Pfeifer, which both give excellent results.

L. DE K.

Proposed Standard Method of Analysis for Zinc. FRANK C. BREYER (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 7—37).—A study has been made of the relative merits of the various methods of zinc analysis, and as a result the following standard method has been devised, which not only gives accurate results for ores and zinc materials of a high degree of impurity, but has also proved satisfactory for the common sulphide and carbonate ores.

The material, 0.5 gram if containing more than 50% of zinc, or 1 gram if containing a smaller proportion, is placed in a 150 c.c. beaker with a little water and 10 c.c. of hydrochloric acid (D 1.20). The beaker is covered, and the mixture boiled for about half an hour. Ten c.c. of sulphuric acid (1:1) are added, and the product is evaporated until fumes of sulphuric acid are produced. The solution is then diluted to 40—50 c.c., and about a gram of powdered aluminium added. The beaker is again covered, and the contents are boiled until colourless. By this means the iron is reduced, and all the metals of the hydrogen sulphide group are precipitated except cadmium. After filtration, 1 c.c. of sulphuric acid (1:1) is added to the filtrate if the cadmium is to be removed electrolytically, the solution diluted to 125 c.c., and electrolysed with 0.8—1 ampere per 100 sq. cm. electrode for one to one and a-half hours at about 3 volts. If the cadmium is to be removed with hydrogen sulphide, 5 c.c. of sulphuric acid (1:1) are added, and after diluting to 100 c.c. hydrogen sulphide is passed rapidly through the solution for fifteen minutes. Dilute ammonia is then added, drop by drop, until yellow cadmium sulphide begins to be precipitated. The solution is heated to 70—90°, the passage of hydrogen sulphide being continued, and then filtered. The precipitate is washed with cold, 8—10% sulphuric acid, and afterwards with hot water. After boiling the filtrate to remove hydrogen sulphide, the solution is cooled, nearly neutralised with potassium hydroxide and sodium hydrogen carbonate, and 2—4 c.c. of 5% sulphuric acid are added. A rapid stream of hydrogen sulphide is then passed through the solution for forty minutes. The zinc sulphide is collected, washed, and then returned to the beaker in which it was precipitated. Hydrochloric acid (10 c.c.) and water are added, and the solution is boiled to remove hydrogen sulphide; 13 c.c. of ammonia (D 0.90) are added, and afterwards neutralised with 3 c.c. of hydrochloric acid (D 1.20); excess of the latter is then added, and the whole diluted to 200 c.c. This solution is titrated with potassium ferrocyanide solution, 1 c.c. of which is equivalent to 10 mg. of zinc, and which has been standardised with amounts of zinc corresponding closely with those present in the sample of ore. The method is much shorter when cadmium is absent or present in quantities of less than 0.05%.

E. G.

Estimation of Zinc and Cadmium. HERMANN WEIL (*Zeitsch. anal. Chem.*, 1913, 52, 549–553).—The author estimates zinc by the well-known titration process with ferrocyanide in presence of ferric tartrate in ammoniacal solution, with dilute acetic acid as external indicator. Cadmium may be estimated similarly, but the author finds that it consumes exactly double the amount of ferrocyanide required by zinc.

When the two metals are both present, a preliminary separation with hydrogen sulphide is recommended; the precipitated cadmium sulphide is then redissolved in boiling dilute hydrochloric acid, oxidised with bromine, and titrated. The filtrate containing the zinc is treated similarly.

Should other heavy metals be present, these must be removed by the usual processes. L. DE K.

Estimation of Small Amounts of Cadmium in the Dry Way. FRANK C. BREYER (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 1–5).—Biewend (A., 1903, ii, 105) has described a method for detecting cadmium in zinc ores by heating 0.1–0.5 gram of the sample in a narrow glass tube with a reducing agent, such as ferrous carbonate, iron, or aluminium. A deposit of cadmium or its oxide is obtained, which can be converted into the characteristic sulphide by igniting it in presence of sulphur vapour.

A modification of this method is described, in which a Rose crucible is substituted for the closed tube. The material to be tested (200 mg.) is placed in the crucible; the Rose stem is introduced so that it nearly touches the substance on the bottom, and a small stream of gas is admitted sufficient to give a flame a quarter of an inch long. The crucible is gradually heated to bright redness, and maintained at this temperature until zinc oxide vapour begins to rise. After the crucible has cooled, a ring or patch of cadmium oxide appears. If the sample contains as little as 0.1% of cadmium, the oxide is plainly visible. As the proportion of cadmium increases, the patch becomes a ring of increasing breadth and thickness. From the appearance of the sublimate, it is possible to judge the amount of cadmium present to within 0.1%, when occurring in quantities of 0.1–0.6%. If 200 mg. of the sample do not yield a brown patch, there is less than 0.1% of cadmium present, and if 400 mg. give a slight coating, between 0.05 and 0.1% is present. Very small traces of cadmium can be estimated by means of Biewend's tube method if the tube is drawn out to a capillary; in this way, 0.001% in ores and light compounds, and 0.0005–0.0001% in spelter and alloys, can be estimated.

Comparison with the usual methods has shown that these new methods give trustworthy results. The methods are chiefly of value as obviating the application of processes for effecting the separation of cadmium in zinc analysis or for estimating cadmium when the metal is either absent or only present in traces. E. G.

Titration of Copper by means of Methanal-sulphurous Acid. PHILIPPE MALVEZIN (*Bull. Soc. chim.*, 1913, [iv], 13, 721–722).—A
53—2

solution for titration is prepared by adding excess of sulphur dioxide to 40% formaldehyde solution and diluting to a suitable concentration. The copper solution is treated with ammonia and titrated with the standard solution until the colour disappears.

J. F. S.

Analysis of Brass. BERTHOLD KÖCH (*Chem. Zeit.*, 1913, 37, 873—874).—A modification of Lunge's process. One grain of turnings is dissolved in a tall, narrow 200 c.c. beaker, covered with a watch-glass, in 10 c.c. of nitric acid (D 1.2), applying a gentle heat. The solution is diluted with 100 c.c. of water, 15 c.c. of dilute sulphuric acid (1:1) are added, and then again water up to 150 c.c. The liquid is then raised to the desired temperature and electrolysed.

With a current of 9 amperes and at 90°, the separation of the copper is complete within twenty to thirty minutes; with 6 amperes and at 70°, in forty minutes; and with 1 ampere and at 50°, in 120 minutes. Wire gauze electrodes are used. The author, however, prefers working with a current of 3 amperes and 3.5 volts at 70—75°; it then takes sixty minutes for complete precipitation. When the electrolysis is finished the electrodes are removed and instantly rinsed with water. The current is then stopped, and after the deposit is washed with alcohol and ether it is dried in an air-bath at 90—100°.

L. DE K.

Electro-analysis of Copper, Antimony, Bismuth, and Tin with Acidified Chloride Electrolytes. EUGENE P. SCHUCH and DENTON J. BROWN (*Eighth Inter. Cong. App. Chem.*, 1912, 21, 81—91).—It has been considered hitherto that solutions of metallic chlorides acidified with hydrochloric acid are unsuitable for electro-analytical work on account of the oxidising action of the chlorine which is liberated. The liberation of chlorine can be prevented, however, by the addition of a suitable reducing agent, and it has been found that copper, antimony, bismuth, and tin can be deposited quantitatively by employing formaldehyde, hydroxylamine hydrochloride, or oxalic acid. In these experiments, the electrolysis was effected with A. Fischer's modification of Sand's electrodes. The deposits are obtained in a satisfactory form, and are probably free from inclusions.

The deposition of tin in presence of hydroxylamine hydrochloride is complete in about ninety minutes at temperatures between 30° and 70° and with a current of 1.5 amperes. This metal can also be estimated by effecting the deposition of the greater part of it in absence of a reducing agent, and then adding ammonium oxalate and oxalic acid; an excellent deposit is thus obtained in about ninety minutes.

Copper can be completely deposited with a cathode potential as low as -0.40 volt against the normal calomel electrode, and this fact renders possible its separation from tin. Both metals can be estimated in the same sample of electrolyte, and the following simple method is recommended for the analysis of bronze. The

alloy is dissolved in aqua regia, and after the solution has been evaporated, 2 grams of hydroxylamine hydrochloride and 5–15 c.c. of hydrochloric acid (D 1.20) are added together with sufficient water to make the total volume 200 c.c. Electrolysis is now effected, the cathode potential being limited to -0.40 volt. The copper is completely deposited in twenty to forty minutes, and the end-point is recognised by the fact that the current must be reduced to zero to prevent the rise of the cathode potential above -0.40 volt. The beaker is lowered from the electrodes, and the latter are washed with a few c.c. of water and the washings added to the electrolyte. The cathode is now detached, rinsed with alcohol and ether, dried quickly, and weighed. This electrode can now be used for the deposition of the tin. A further quantity of hydroxylamine hydrochloride (3 grams) is added to the solution, and the latter treated with a constant current of 1.5 amperes. The deposition of the tin is complete in twenty to forty minutes.

Antimony can be estimated in solutions acidified with hydrochloric acid if hydroxylamine hydrochloride is added, the solution heated to 50 – 75° , and the cathode potential limited to -0.40 volt. Bismuth can be estimated in a similar manner, but in order to obtain a good deposit, the cathode potential should be limited to -0.25 volt until most of the metal has separated, and then gradually raised until it reaches -0.60 volt. Both antimony and bismuth are deposited completely in a few minutes. E. G.

New Method for the Analytical and Quantitative Separation of Mercury from Bismuth. ADOLFO P. CASTAÑARES (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 39–40).—Mercury and bismuth can be separated with great precision by taking advantage of the fact that mercury is not precipitated by ammonium carbonate from hot solutions of mercuric compounds strongly acidified with nitric acid, whilst under similar conditions bismuth is totally precipitated.

The concentration of the mercury in the solution should not much exceed 0.1%. To the solution containing both metals, nitric acid (D 1.42) is added in a quantity of 5 c.c. per 100 c.c. of solution, and the mixture is heated to 60° . Solution of ammonium carbonate (10%), containing 1% of ammonia, is slowly added until the liquid is decidedly alkaline. The mixture is now heated at 80° until carbon dioxide ceases to be evolved. The precipitate is collected in a Gooch crucible, washed with 1% solution of ammonia, dried at 100° , and heated to redness until of constant weight.

If the solution contains chlorides, the precipitate obtained on adding ammonium carbonate must be collected, dissolved in dilute nitric acid, and the solution evaporated. The residue must be treated three or four times with concentrated nitric acid, and evaporated each time on the water-bath in order to convert the bismuth into the form of nitrate, which can then be precipitated by ammonium carbonate or phosphate.

In either case, the filtrate containing the mercury is warmed, treated with a slight excess of freshly prepared ammonium sulphide, and boiled for a few minutes. The precipitate is collected in a

Gooch crucible, washed first with water containing ammonium sulphide, and afterwards with alcohol, and dried at 100–110°. The mercuric sulphide is thus obtained free from sulphur, and therefore does not require to be treated with carbon disulphide.

The method is simple, rapid, and accurate.

E. G.

Gravimetric Estimation of Tungsten, Chromium, Silicon, Nickel, Molybdenum, and Vanadium in Steels. S. ZINBERG (*Zeitsch. anal. Chem.*, 1913, 52, 529–534).—One gram of the sample is dissolved in dilute hydrochloric acid (1:4), and then heated to boiling with addition of a few c.c. of nitric acid; residue, tungstic acid. The silica is recovered from the solution by evaporation with 6 c.c. of sulphuric acid. The filtrate from the silica is treated under pressure with hydrogen sulphide; this precipitates molybdenum sulphide, convertible into oxide by ignition. The filtrate is concentrated by evaporation, oxidised with nitric acid, and poured into a boiling solution of sodium hydroxide (10 grams to 200 c.c. of water). Iron, chromium, and nickel are precipitated completely; the filtrate contains the vanadium and traces of chromate. After acidifying with nitric acid, a hot solution of barium nitrate is added in slight excess. The filtrate is then evaporated to dryness with addition of a few drops of alcohol. Water is added, and the chromium precipitated with a little ammonia; the precipitate is then added to the iron precipitate, the whole is dissolved in nitric acid, evaporated with potassium chlorate, and the chromium precipitated as usual with mercurous nitrate.

The ammoniacal filtrate contains the vanadium, which, after expelling the free ammonia, may be precipitated by a faintly acid solution of mercurous nitrate. The precipitate settles better if a drop of ammonia is next added, and may then be ignited to oxide.

Nickel is best tested for separately. After eliminating the tungsten as directed, the filtrate is mixed with 2 grams of tartaric acid, ammonia is added in slight excess, and the nickel precipitated at 70–80° by addition of 15–25 c.c. of a 1% solution of dimethylglyoxime; the precipitate is then converted by ignition into nickelous oxide.

In the absence of molybdenum and tungsten, the chromium and vanadium may be isolated by converting the iron into nitrate and fusing the dry mass with 2–3 grams of sodium potassium carbonate. Any nickel remains insoluble on lixiviating the fused mass.

L. DE K.

Estimation of Tungstic Acid and Silicic Acid. HUGO HERMANN (*Zeitsch. anal. Chem.*, 1913, 52, 557–568).—The separation of tungstic acid by Scheele's method by precipitation with nitric acid succeeds best with the ortho-compound. Para- and meta-compounds should therefore be rendered alkaline at first.

In presence of silicic acid, considerable amounts of silico-tungstic acids may form even in the cold, so that a portion of the tungstic acid is not separated. Even carbon dioxide will cause this. Silico-

tungstic acid, once formed, can only be resolved by prolonged warming in strongly alkaline solutions.

The formation of these complex acids may be prevented by adding an excess of nitric acid suddenly.

The conversion of silicic acid into silico-tungstic acid renders possible its quantitative estimation with great accuracy. The characteristic precipitate yielded by that acid with luteocobalt solution serves as a microscopical test for silica. L. DE K.

Separation of Tungsten from Thorium, Lanthanum, Cerium, Erbium, Didymium or Silica. MAX WUNDER and A. SCHAPIRA (*Ann. Chim. anal.*, 1913, 18, 257—260).—*Separation of the Oxides of Tungsten and Thorium.*—The oxides (about 0.35 gram) are fused over the blowpipe with 5 grams of sodium carbonate for one hour. The mass is boiled with water for twenty minutes, and the residue washed with hot water containing a little sodium carbonate. After washing the thorium oxide with 5% hydrochloric acid, it is ignited and weighed. From the filtrate, the tungsten is recovered by acidifying with nitric acid and precipitating as mercurous tungstate, which is then ignited to oxide.

Oxides of Tungsten and Lanthanum.—The process is exactly the same as for thorium.

Oxides of Tungsten and Cerium.—The mixture cannot be ignited without loss; after fusion with sodium carbonate, the cerium remains insoluble, and is treated as directed for thorium. The same applies to *tungsten* and *erbium*, with this difference, that the latter oxide dissolves in 5% hydrochloric acid, and must be reprecipitated with ammonia.

Tungsten and Didymium.—On ignition, volatilisation takes place, but on fusion with sodium carbonate and filtering the solution (as in the case of erbium) when cold, the oxide of didymium remains insoluble, and is purified by dissolving in 5% hydrochloric acid and reprecipitation with ammonia.

Oxide of Tungsten and Silica.—This is a more troublesome process. The fusion (including alumina) is dissolved in boiling water, and then boiled with an excess of ammonium nitrate, which precipitates the alumina and part of the silica; after igniting and weighing, the silica is removed by means of hydrofluoric acid and a few drops of sulphuric acid, and found from the loss. The filtrate is then precipitated with mercurous nitrate; the precipitate, after ignition, consists of tungstic acid and some silica, which is then removed by means of hydrofluoric acid as directed. The filtrate from the mercurous tungstate still contains silica, which is recovered by evaporation, drying of the residue at 110°, and treating this with dilute nitric acid. L. DE K.

Estimation of Paraffin in Native Asphalt and Petroleum Asphalt. J. MAREK (*Zeitsch. anal. Chem.*, 1913, 52, 553—556).—One gram of the sample is dissolved in 2 c.c. of chloroform, 50 c.c. of light petroleum (b. p. 70°) are added, and after an hour the solution is filtered through cotton wool moistened with light

petroleum, and covered with 40–60 grams of powdered animal charcoal. The mass is then washed thrice with 30 c.c. of light petroleum. The liquid is distilled off, and the residue dissolved in 10 c.c. of ether. After adding 10 c.c. of absolute alcohol and cooling to -20° , the paraffin is collected; a special apparatus for cooling and filtering is described and figured.

Of asphaltic stones, a larger quantity is taken, and the powder heated to boiling with 50 c.c. of light petroleum. When cold, the solution is decolorised as described for asphalt. L. DE K.

Identification of Hydrocarbons of the Benzene Series. H. ROSSER (*Ann. Chim. anal.*, 1913, 18, 260–262).—The members of the benzene series may be distinguished from those of the methane series by the miscibility test with alcohol. Whereas a satisfactory reading will be obtained on heating 5 c.c. of light petroleum with 5 c.c. of alcohol, it is necessary to take 10 c.c. of xylene, toluene, or commercial benzene, and 15 c.c. of pure benzene, in order to ensure a good reading. Mixtures may thus be recognised (compare also this vol., ii, 353). L. DE K.

The Oxidation Assay of Essential Oils. FRANCIS D. DODGE (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 86–92).—The stability of the constituents of essential oils towards cold permanganate is described. Camphor, fenchone, bornyl acetate, eucalyptol, paraffins and aliphatic ketones are the only common substances which remain unaffected. In some cases, as with borneol and fenchyl alcohol for example, the oxidation is limited to the formation of a stable ketone, but, generally speaking, the destruction is complete. Phenolic ethers exhibit peculiarities. Anethole and methylchavicol yield anisic acid, methyleugenol and isomethyleugenol give veratric acid, but the methylene ethers, as, for example, safrole and *iso*-safrole, are completely oxidised.

For practical purposes a measured volume (10 c.c.) of the oil is run into a narrow-necked litre-flask, and shaken with small portions of concentrated potassium permanganate in the cold until the colour is permanent during a few hours. Sulphurous acid is then carefully added to dissolve the precipitate, and the oil is allowed to rise and is finally measured. The process may be applied to the detection of petroleum products in turpentine or Ceylon citronella oil, and to the differentiation between bornyl acetate and its isomerides. Hesse and Müller used the same method for separating benzyl and linalyl acetates (*A.*, 1899, i, 441). J. C. W.

Direct Estimation of Caoutchouc Applicable to Specifications on Vulcanised Rubber Goods. CHARLES R. BOGGS (*Eighth Inter. Cong. App. Chem.*, 1912, 9, 45–58).—The method proposed is a modification of the bromination process described originally by Budde (*Gummi Zeit.*, 1907, 21, 1205). The sample is ground to pass a 20-mesh sieve, extracted with acetone, and dried in an atmosphere free from oxygen. A quantity of about 0.1 gram of the powder is then boiled for three hours with 20 c.c. of toluene,

the greater part of the latter is then removed by evaporation on the water-bath, and, after the addition of 50 c.c. of carbon tetrachloride, the cold mixture is treated with 50 c.c. of a solution containing 16 grams of bromine and 1 gram of iodine in 1 litre of carbon tetrachloride. After twenty-four hours, 50 c.c. of absolute alcohol are added, and, after the lapse of a further sixteen hours, the precipitate is collected on a filter, washed with a mixture consisting of 2 vols. of carbon tetrachloride and 1 vol. of alcohol, then with alcohol, boiling water, and again with alcohol. The air-dried precipitate is ignited with a large excess of sodium carbonate and potassium nitrate, and the bromide is estimated in the usual way. The amount of bromine found is multiplied by the factor 0.425 to give the quantity of caoutchouc. No correction is applied for the sulphur in the bromide.

W. P. S.

New Method for the Identification of Methyl Alcohol. PAUL N. RAIKOW (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 417—419).—When a solution of nitromethane is treated with ammonia, and solution of sodium nitroprusside is added drop by drop, an intense indigo-blue coloration is produced even if only traces of nitromethane are present. The blue colour gradually changes through green to yellow or yellowish-red. On further addition of the sodium nitroprusside solution, the blue colour is restored and again fades; this reappearance and disappearance of the blue colour can be repeatedly effected. If the higher nitro-paraffins and acetone are treated in this way, only cherry-red colorations are produced.

This reaction has been applied to the detection of methyl alcohol in ethyl alcohol. About 200 c.c. of the ethyl alcohol are acidified with phosphoric acid and submitted to distillation with the aid of a fractionating column. The first 10 c.c. of distillate are placed in a 60 c.c. flask with 4 grams of red phosphorus. A reflux condenser is attached, and 25 grams of iodine are gradually added. After twenty minutes the mixture is fractionated, and the first 5 c.c. of distillate are treated with 2—3 grams of silver nitrite and slowly distilled to dryness. The distillate is collected in quantities of 3—4 drops, and these are tested for nitromethane by the method already described.

E. G.

Detection and Estimation of Methyl Alcohol. ROLAND SCHMIDEL (*Pharm. Zentr.-h.*, 1913, 54, 709—716).—The method proposed for the detection of methyl alcohol in the presence of ethyl alcohol consists in rendering the mixture of alcohols alkaline, and adding dilute hydrogen peroxide in small quantities at a time; the oxidation must be carried out at a temperature of about 50°, and under these conditions methyl alcohol is converted into formic acid, ethyl alcohol yielding acetic acid. The presence of the former acid is then detected by its reducing properties. The method may be rendered quantitative by distilling the acids with steam, collecting the acid distillate in calcium carbonate, and eventually estimating the formic acid by the mercuric chloride

process. Each gram of mercurous chloride obtained corresponds with 0.0678 gram of methyl alcohol.

W. P. S.

Estimation and Detection of Methyl Alcohol. THEODORE VON FELLEBERG (*Chem. Zentr.*, 1913, ii, 309—310; from *Mitt. Lebensmittelsunters. Hyg.*, 1913, 4, 122—146).—When 40% methyl alcohol is shaken with an equal volume of ether, the aqueous-alcoholic layer increases in volume, whilst the ethereal layer diminishes. With ethyl alcohol of similar strength, the reverse is the case, the aqueous-alcoholic layer decreasing. When 50 c.c. of each liquid are used at 15°, the increase is +4.15 in the case of methyl alcohol, and the decrease is -6.48 for ethyl alcohol. Mixtures of the two alcohols give intermediate values, from which their proportions can be calculated. In analysing spirits the aldehydes, esters, terpenes, etc., have first to be removed. Mixtures of pure alcohols can be analysed with an error of only 0.2—0.4%. For the detection of methyl alcohol, Denigès' (A., 1910, ii, 461) method is considered the best. Ethyl alcohol and the higher homologues may be salted out from admixture with methyl alcohol by means of potassium carbonate, so enriching the solution with methyl alcohol that it becomes possible to detect 1 part in 100,000.

E. F. A.

Estimation and Detection of Small Quantities of Methyl Alcohol in the Blood and Tissues. MAURICE NICLOUX (*Eighth Inter. Cong. App. Chem.*, 1912, 19, 259—260).—The tissues are minced into 6—8 times the weight of saturated picric acid solution, and a fifth of the bulk of the liquid is then distilled off. The addition of picric acid prevents frothing. The methyl alcohol is estimated by means of potassium dichromate solution by the same process as that employed by the author for the estimation of ethyl alcohol. The methyl alcohol is further characterised by determining the amount of carbon dioxide formed in the reaction and the CO_2/O_2 ratio, which for this alcohol is 0.915.

S. B. S.

Gabriel Bertrand's Method of Sugar Estimation. G. SONNTAG (*Biochem. Zeitsch.*, 1913, 53, 501—503).—The author calls attention to the fact that the principles involved in what is now generally known as Bertrand's process were already suggested by Schwarz in 1852, and actually employed by Mohr for dextrose estimation in 1873, and by the author himself in a form only slightly differing from that used by Bertrand in 1903. His experimental method is recapitulated; and it is claimed that it is as feasible as that of Bertrand.

S. B. S.

Electrolytic Apparatus for Use in Invert Sugar Estimations. B. B. ROSS (*Eighth Inter. Cong. App. Chem.*, 1912, 8, 75—77).—The cuprous oxide obtained in the usual way by boiling the invert sugar solution with an excess of Fehling's solution is collected on a small asbestos filter contained in a tapped funnel. The cuprous

oxide is washed with hot water and then dissolved by filling the funnel (after closing the tap) about three-fourths full with nitric acid (4 c.c. of nitric acid, D 1.42 per 100 c.c. of water). A platinum cylinder is then immersed in the solution, and serves as the cathode, whilst a platinum spiral fused through the funnel just above the tap acts as the anode, and the copper is deposited on the cathode by the application of a current of suitable density. The deposited copper is, finally, dried and weighed on the cathode. W. P. S.

Estimation of Cellulose by means of Nitric Acid. VENKATA RAO and BERNHARD TOLLENS (*J. Landw.*, 1913, 61, 237—244).—Comparative estimations of cellulose in various substances by the nitric acid method proposed by Dmochowski and Tollens (A., 1910, ii, 554) and by the chlorine process described by Cross and Bevan (T., 1889, 55, 199) showed that the factor 1.1 given by Dmochowski and Tollens is not applicable in every case. A slightly different factor has to be used for various classes of substances in order that the results obtained by the nitric acid method may agree with those found by the chlorine process. For instance, in the case of jute, the factor is 1.16, for buckwheat flour, 1.30, cocoa husk, 1.19, and cotton-wool, 0.98. W. P. S.

Impossibility of Separating Tartrate and Free Tartaric Acid in Wine. W. I. BARAGIOLA (*Chem. Zentr.*, 1913, ii, 179; from *Schweiz. Woch. Chem. Pharm.*, 1913, 51, 289—291. Compare Baragiola and Godet, A., 1912, ii, 981).—Since wine represents a solution in which there is equilibrium between the free and fixed tartaric acid, it is obvious that the slightest disturbance of the conditions with the object of analytical determination of the acid will change the equilibrium. It is possible only to determine the total tartaric acid, and calculate its state of combination on physico-chemical data when all the acids and all the bases have been determined. Calculations based on the total, the soluble and insoluble alkalinity of the ash lead to incorrect results. E. F. A.

Estimation of Tartaric Acid. PAUL B. DUNBAR (*Eighth Inter Cong. App. Chem.*, 1912, 26, 361—373).—It has been shown by Dunbar and Bacon (A., 1912, ii, 699) that malic acid can be estimated by measuring the increase in rotation produced by treating the solution with uranyl acetate. It was pointed out that the specific rotation of *d*-tartaric acid is also increased by uranium salts, and that the presence of this acid therefore interferes with the estimation of malic acid. The present work was undertaken with the object of devising a method for estimating tartaric acid, and which could be applied to the estimation of both malic and tartaric acids in the same solution. In this paper an account is given of a method for estimating tartaric acid.

If a solution of tartaric acid or tartrates containing from 0.2 to 3.0 grams of the acid per 100 c.c. is treated with uranyl acetate, each gram of acid in 100 c.c. produces a rotation of $+19.6^\circ$ F, the ratio of tartaric acid concentration to rotation being 0.051. Hence,

in the absence of malic acid, tartaric acid can be estimated by treating the solution with uranyl acetate, polarising, and multiplying the reading by 0.051. In presence of other optically active substances, a portion of the solution must be freed from tartaric acid by precipitation with lead acetate and polarised separately. The difference between this reading and that obtained with the solution treated with uranyl acetate gives the polarisation due to the uranyl tartaric complex.

E. G.

Estimation of Malic and Tartaric Acids in the Same Solutions. PAUL B. DUNBAR (*Eighth Inter. Cong. App. Chem.*, 1912, 26, 375—385).—Dunbar and Bacon (A., 1912, ii, 699) and Dunbar (preceding abstract) have shown that malic and tartaric acids, when occurring separately, can be estimated by observing the increase in rotation produced on treating the solutions with uranyl acetate.

A method has now been devised for estimating both acids in the same solution, which is based on the facts: (1) that the rotations of both acids are increased independently by treatment with uranyl acetate under definite conditions, and (2) that both acids can be oxidised quantitatively to oxalic acid by heating with potassium permanganate in alkaline solution. When determinations have been made of the total rotation produced on addition of uranyl acetate, and the amount of oxalic acid formed on oxidation or the quantity of permanganate reduced, the amounts of malic and tartaric acids present can be calculated. The method is interfered with by the presence of substances which form oxalic acid on oxidation, and which cannot be removed before treatment with the permanganate.

E. G.

The Significance of the Marchi Reaction. W. CRAMER, HENRY O. FEISS, and W. E. BULLOCK (*Proc. physiol. Soc.*, 1913, li—lii; *J. Physiol.*, 46).—In the degeneration of nerve-fibres, ordinary fats, but no cholesterol esters are formed; it is the ordinary unsaturated fat that is responsible for the Marchi reaction, for which it is a specific stain. The method can be applied to ascertain microchemically the composition of fat droplets in cells.

W. D. H.

Detection of Acetaldehyde in Paracetaldehyde. II. GEORGE HEYL (*Chem. Zentr.*, 1913, ii, 85; from *Apoth. Zeit.*, 1913, 28, 306—307. Compare this vol., ii, 636).—When 6 c.c. of paracetaldehyde are shaken with a mixture of 2 c.c. of potassium hydroxide and 4 c.c. of water, the aqueous layer should not become yellow or brown within an hour; 0.2% of acetaldehyde is enough to give a positive reaction, and some pure commercial preparations of paracetaldehyde also give the reaction. Ten c.c. of a 2.5% aqueous solution of paracetaldehyde, when shaken with 20 drops of a freshly prepared 1% solution of sodium nitroprusside and 3 drops of piperidine, should not give a blue coloration.

E. F. A.

Estimation of Benzaldehyde and Oil of Bitter Almond. FRANCIS D. DODGE (*Eighth Inter. Cong. App. Chem.*, 1912, 17, 15—20).—Of the various methods which have been proposed for

the estimation of aldehydes, Denner's hydrazone method, Bennett's oxime method (A., 1909, ii, 192), and the sodium hydrogen sulphite method yield trustworthy results in the case of benzaldehyde. It is essential, however, in the latter method, to maintain the temperature of the reacting substances at 0° ; the time of contact of the benzaldehyde with the sodium hydrogen sulphite solution should be two hours. Approximately correct results may also be obtained by a method which is based on the reaction between benzaldehyde and potassium hydroxide according to the equation: $2C_6H_5 \cdot CHO + KOH = C_6H_5 \cdot CO_2K + C_6H_5 \cdot CH_2 \cdot OH$. The benzaldehyde is treated with an excess of 2.5*N*-potassium hydroxide solution, and, after remaining for twenty-four hours, the excess is titrated with *N*/2-hydrochloric acid. The presence of hydrocyanic acid interferes to some extent when any of these methods is applied to the estimation of benzaldehyde in oil of bitter almonds. The author has isolated about 0.2% of a heavy yellow oil from natural benzaldehyde; the nature of this oil has not been ascertained, but it is probable that it has some influence on the aroma of the natural oil.

W. P. S.

Detection of Ionone. MAURICE HANRIOT (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 373—374).—If ionone is dissolved in concentrated hydrochloric acid, an intense golden-yellow coloration is produced; on adding chloral hydrate and heating the mixture, the liquid becomes dull violet. If the solution, when cold, is shaken with ether, it is decolorised, and on evaporating the ethereal solution, a violet substance is obtained which is soluble in water and is immediately decolorised by ether. *iso*Ionone gives the same reaction, and it is probable that it takes place with ionone only after the latter has been transformed into *iso*ionone by the hydrochloric acid. ψ -Ionone and natural essence of violets do not respond to the test. The test is of value for the detection of ionone in commercial perfumes, and does not seem to be interfered with by the presence of natural essences.

E. G.

Estimation of Urea in Blood by means of Sodium Hypobromite (Mercury and Water Ureometers). ANDRÉ GUILLAUMIN (*J. Pharm. Chim.*, 1913, [vii], 8, 64—70).—Small quantities of urea present in blood may be estimated equally accurately by the sodium hypobromite method, using either a mercury or water ureometer to measure the gas liberated.

E. F. A.

Estimation of Urea. JOHN ALEXANDER MILROY (*Biochem. J.*, 1913, 7, 399—409).—The procedure is as follows. The phosphates present in the sample of urine are removed by precipitation with baryta mixture. Twenty-five c.c. of the filtered urine are titrated with *N*/10-hydrochloric acid until neutral to methyl-red, 5 c.c. of neutral formaldehyde are added, and the titration with decinormal alkali is completed. This gives the approximate amount of nitrogen in the form of pre-formed ammonia and amino-acids.

Ten c.c. portions of the filtrate are heated with 8 c.c. of *N*-sulphuric acid at 155° for 1.5 hours in an autoclave. After filtering, the formaldehyde titration is effected in the usual manner; it gives the pre-formed ammonia and amino-acids above, for which deduction can be made, together with amino-acids set free by hydrolysis and the ammonia derived from the urea. The distillation methods give the pre-formed ammonia and that formed by hydrolysis of urea. Comparative experiments show the formaldehyde titration method to give a positive error of 1.7% of urea, but it has the advantage of being quicker and giving at the same time an approximate estimate of the pre-formed ammonia and amino-acids.

E. F. A.

Cadmium Nitrate in Qualitative Analysis. ANTON VORISEK (*Eighth Inter. Cong. App. Chem.*, 1912, 17, 91—102).—Cadmium nitrate may be employed in the analysis of the second group of anions to remove S, $\text{Fe}''(\text{CN})_6$, and $\text{Fe}'''(\text{CN})_6$. The minimum amounts of cadmium nitrate and potassium hydroxide required for a complete precipitation were ascertained; for instance, at least 6.7 c.c. of *N*/5-cadmium nitrate solution and 2 c.c. of *N*/5-potassium hydroxide solution must be used for 10 c.c. of *N*/10-potassium ferrocyanide solution. The amount of potassium hydroxide consumed is out of proportion to the acidity of the cadmium solution, and the alkali evidently takes part in the formation of the precipitates. Of the cyanogen ions more than 80% remain unprecipitated, so that cyanogen ions may be detected in the filtrate from the cadmium precipitate and apart from $\text{Fe}''(\text{CN})_6$ and $\text{Fe}'''(\text{CN})_6$. A procedure for the subdivision of the anions of the second group is outlined.

Ammonium acetate and thiocyanate are the most effective ammonium salts for preventing the precipitation of calcium tartrate. Tartaric and citric acids may be precipitated completely from neutral solutions by cadmium nitrate and potassium hydroxide. In the case of tartaric acid, 10 c.c. of the *N*/5-solution require at least 22 c.c. of *N*/5-cadmium nitrate solution and 11 c.c. of *N*/8-potassium hydroxide solution, whilst an equivalent quantity of citric acid requires 11.2 c.c. of cadmium nitrate and 2.2 c.c. of potassium hydroxide. The precipitate formed with tartaric acid appears to have the formula $\text{Cd}_2(\text{OH})_2\text{C}_4\text{H}_4\text{O}_6$, but with citric acid the results failed to indicate an agreement with any one of the formulae extant. A process for the detection of these two acids and the removal of certain ions of the second group in one treatment is given.

W. P. S.

Micro-sublimation of Alkaloids under Reduced Pressure. R. EDER (*Chem. Zentr.*, 1913, ii, 91—92; from *Schweiz. Woch. Chem. Pharm.*, 1913, 51, 228—231, 241—245, 253—256).—A simple apparatus is described which allows the determination of the temperature of sublimation under 10 mm. pressure. The sublimation points of the pure alkaloids are as follows: Cocaine, 75—90°;

atropine, 93—110°; codeine, 100—130°; quinine, 133—148°; narcotine, 146—156°; brucine, 158—175°; solanine, 168—174°. The sublimate was studied with the lens during formation, and their crystallographic appearance and microchemical reactions noted. The alkaloids are classified as follows:

A. Those which sublime without melting. 1. Caffeine, theobromine, cinchonine, solanine, cantharidine give direct crystalline sublimate. 2. A number of alkaloids give at first a homogeneous sublimate, consisting of minute, amorphous droplets, which subsequently becomes crystalline as the layer thickens. 3. Others give a deposit in which sometimes irregular crystals appear subsequently, or it remains amorphous.

B. 4. Those which give a sublimate above their melting point, consisting either of minute, amorphous droplets or crystals, for example, narceine, pilocarpine, veratrine, emetine, colchicine.

C. 5. Sparteine sulphate and nicotine hydrochloride give no sublimate on account of dissociation or decomposition.

The stability of the amorphous droplets is smaller, and the crystallisation takes place more easily and quickly the lower the compound sublimes below its melting point, that is to say, the higher the vapour pressure of the alkaloid. Compounds in group 1 above have a high vapour pressure, and therefore are crystalline from the start. In group 2 the vapour pressure is lower, and crystallisation takes place with difficulty. In groups 3 and 4 the vapour pressure is still lower, and crystallisation is only occasional.

E. F. A.

Estimation of Uric Acid in Urine. FRANZ HERLES (*Fifth Inter. Cong. App. Chem.*, 1912, 19, 141—144).—The principle of this quick process consists in precipitating the urate by ammonium chloride as ammonium salt, according to the method of Hopkins and others, treating this precipitate with excess of *N*/10-sulphuric acid, and estimating the excess of acid added by titration with alkalis, using methyl-orange as an indicator, as this is not affected by the uric acid. One c.c. of *N*/10-acid is equivalent to 0.01682 gram of uric acid. If the urine is not clear, the uric acid precipitate is dissolved in water with addition of alkali, sufficient of which must be added to produce a red colour with phenolphthalein, the mixture is heated, made up to a definite bulk, and an aliquot part is filtered off from the phosphates precipitated. In this portion the uric acid is estimated by the method described above.

S. B. S.

The Chemical Nature of Substances from Alcoholic Extracts of Various Foodstuffs which Give a Colour Reaction with Phosphotungstic and Phosphomolybdic Acids. CASIMIR FUNK and A. BRUCE MACALLUM (*Biochem. J.*, 1913, 7, 356—358).—Folin and Macallum (*A.*, 1912, ii, 495; this vol., ii, 80) introduced a phosphotungstic acid solution as a colour reagent for uric acid, and Folin and Denis (*A.*, 1912, ii, 1011) a mixture of phosphotungstic and phosphomolybdic acids for polyphenols.

The action on a large number of related substances of the two reagents was investigated. The uric acid reagent gives a reaction with certain purine and tyrosine derivatives, and the polyphenol reagent appears to be specific for purine derivatives and polyphenols. Amino-acids, polypeptides, and diketopiperazines are negative to both reagents. The replacement of one hydrogen atom in the purine ring lessens or abolishes the uric acid reaction. In the case of the phenol reagent this occurs when two hydrogen atoms are replaced.

The alcoholic extracts of different foodstuffs rich in vitamins give both reactions markedly; as the vitamin fractions are purified the reactions gradually disappear, and their curative power for polyneuritis lessens. The reactions are sensitive, and so may be used to ascertain the purity of phosphatides, caseinogen, and other food products.

W. D. H.

Estimation of Aspirin. A. ASTRUC (*J. Pharm. Chim.*, 1913, [vii], 8, 5—8).—To verify the purity of aspirin, it is proposed first to titrate 1.8 grams with *N*-potassium hydroxide solution in presence of phenolphthalein, and secondly to saponify with alcoholic potassium hydroxide and show that double the former quantity of alkali is required.

E. F. A.

Detection of Bile Pigments in Urine. C. J. REICHARDT (*Pharm. Zeit.*, 1913, 58, 591—592).—Attention is drawn to the fact that very dark-coloured urines fail to give a positive reaction with Gmelin's test. Only when the urine has been exposed to air and light, and probably to bacterial decomposition, the bilirubin oxidised to biliverdin, and the chromogens and indigo compounds reduced, is it possible to detect the presence of bile pigments.

W. P. S.

The Separation of Cystine and Tyrosine. R. H. ADERS PLIMMER (*Biochem. J.*, 1913, 7, 311—317).—Cystine and tyrosine can be separated by means of phosphotungstic acid; the precipitation of cystine is almost complete, but loss occurs in its recovery from the precipitate; almost the whole of the tyrosine can be recovered from the filtrate and washings. The two substances can be imperfectly separated by mercuric sulphate in 5% sulphuric acid; the cystine is not completely precipitated, and the tyrosine which is recovered is impure. A complete and quantitative separation can be brought about by absolute alcohol saturated with hydrogen chloride. The tyrosine is rapidly converted into tyrosine ester, and goes into solution. It can be recovered by boiling the solution when diluted with water, and then neutralising with ammonia. Almost the whole of the cystine is insoluble; the portion which goes into solution is precipitated by adding an equal volume of absolute alcohol. The cystine is not converted into its ethyl ester, since after dissolving the insoluble portion in dilute hydrochloric acid, it is precipitated in typical crystals on the addition of ammonia.

W. D. H.

The Estimation of Tyrosine in Proteins by Bromination. R. H. ADERS PLIMMER and (Miss) ELIZABETH C. EAVES (*Biochem. J.*, 1913, 7, 297—310).—The estimation of small quantities of tyrosine can be effected by Millar's method of bromination, but it is preferable to add excess, and titrate the non-absorbed halogen with thiosulphate solution. Tyrosine cannot be directly estimated in the presence of protein, because tryptophan and histidine both absorb bromine; the latter can be removed by precipitation with phosphotungstic acid. The absorption of bromine by tryptophan is not wholly eliminated after boiling with acid, so that tyrosine cannot be estimated by this method in solutions containing the products of acid hydrolysis which contain tryptophan. Values for the tyrosine content of proteins, agreeing with those obtained by isolation and weighing, are obtained when the bromine absorption of a tryptic digest is measured after an interval of about six hours.

W. D. H.

Estimation of Tryptophan in Protein. JESSE A. SANDERS and CLARENCE E. MAY (*Biochem. Bull.*, 1913, 2, 373—378).—The method recommended is, in outline, to subject the proteins to pancreatic digestion, inoculate the digest with faecal bacteria, and estimate the indole liberated colorimetrically.

W. D. H.

Hopkins and Cole's Modification of the Adamkiewicz Test for Protein. VERNON H. MOTTRAM (*Biochem. J.*, 1913, 7, 249—259).—This test fails in the presence of small amounts of oxidising agents, but traces of these improve the reaction when pure sulphuric acid is used. With commercial sulphuric acid the result is probably due to oxidising agents contained in it. The reaction rate is increased by temperature.

W. D. H.

The Estimation of Albumin-Nitrogen, Ovomuroid-Nitrogen, Free and Combined Carbohydrates in the White of Incubated Eggs. HUBERT W. BYWATERS (*Proc. physiol. Soc.*, 1913, xxxv—xxxvi; *J. Physiol.*, 46).—Total nitrogen is estimated by Kjeldahl's method. The egg-white is then diluted, and heat coagulated after appropriate acidification; the ovomucoid nitrogen is estimated in the filtrate and washings, so also is the sugar; when ovomucoid is boiled with 5% hydrochloric acid, the sugar in combination is set free, and this is estimated by Pavy's method.

W. D. H.

The Behaviour of Blood with Hydrazine Hydrate. GEORGE A. BUCKMASTER (*Proc. physiol. Soc.*, 1913, xlviii—xlix; *J. Physiol.*, 46).—Hydrazine hydrate reduces oxyhæmoglobin, and nitrogen is evolved in exactly equivalent volume to that of the oxygen removed. No other constituent of the blood does this. If the quantity of oxygen evolved by the ferricyanide method is measured, it is equal to that of nitrogen evolved by hydrazine hydrate, but the latter reagent does not liberate carbon monoxide from carboxy-

hæmoglobin as ferricyanide does, nor is there any liberation of gas from reduced hæmoglobin. It is therefore possible in a given sample of blood to determine the relative quantities of oxyhæmoglobin, carboxyhæmoglobin, and reduced hæmoglobin.

W. D. H.

Evaluation of Medicinal Papain Preparations. R. DELAUNAY and O. BAILLY (*Chem. Zentr.*, 1913, i, 1895—1896; from *Bull. Soc. Pharmacol.*, 20, 141—147).—When allowed to act for six hours, papain behaves as a peptonising enzyme, and only as a very weak peptolysing enzyme. It dissolves and hydrolyses coagulated proteins, such as fibrin, forming filtrates which are no longer precipitated on the addition of nitric acid, and have a low amino-index. Papain thus resembles pepsin, but differs in that the optimum temperature is about 80°, and the medium must have a neutral or faintly alkaline reaction. Papain differs from pancreatin in its low peptolysing powers. To evaluate papain, the amount of fibrin which passes into solution in a given time under the conditions of maximum activity is determined. The disappearance of the power of nitric acid to cause a precipitate or the alteration in the amino-index are not trustworthy indications of the activity of papain.

E. F. A.

General and Physical Chemistry.

Rotatory Dispersion of Free *l*-Bornylxanthic Acid. LEO TSCHUGAEV (*Bull. Soc. chim.*, 1913, [iv], 13, 793—796).—The necessary ethereal solutions of *l*-bornylxanthic acid are obtained by dissolving a known quantity of sodium *l*-bornylxanthate in water, washing the solution with ether, cooling with ice, acidifying with a slight excess of sulphuric acid, and extracting with ether. A series of experiments has been made at definite intervals of time for the rays $\lambda = 656, 589, 527, \text{ and } 499 \mu\mu$.

The free acid is levorotatory for all wave-lengths, and also exhibits abnormal rotatory dispersion. The values corresponding with the red end of the spectrum diminish progressively with the time, whilst those corresponding with the green and blue end increase. Consequently, the maximum of rotation becomes displaced towards the violet portion of the spectrum, and the abnormal dispersion is gradually replaced by that characteristic of borneol, and, more generally, of substances possessing normal dispersion. This is attributed to the decomposition of *l*-bornylxanthic acid into *l*-borneol and carbon disulphide. H. W.

Rotatory Dispersion of Certain Derivatives of β -Pinene (Nopinene). LEO TSCHUGAEV and A. KIRPETCHEV (*Bull. Soc. chim.*, 1913, [iv], 13, 796—803).—The present work has been undertaken to test the previous conclusion (Tschugaev, A., 1912, ii, 822) that, whilst optically active alcohols generally have normal dispersion-coefficients, the ratio α_F/α_C for hydroaromatic ketones rises to 3.5, and, further, that this exaltation is connected with the selective absorption in the ultra-violet portion of the spectra of the latter.

Nopic acid (compare Wallach and Blumann, A., 1907, i, 936), when dissolved in alcohol ($c = 2.655$), has $[\alpha]_C - 11.41^\circ$, $[\alpha]_D - 14.46^\circ$, $[\alpha]_E - 18.53^\circ$, $[\alpha]_F - 22.60^\circ$, $[\alpha]_F/[\alpha]_C 1.98^\circ$.

Nopinol, m. p. $101-102^\circ$ (Wallach and Blumann's α -nopinol), has $[\alpha]_C^{20} - 7.01^\circ$, $[\alpha]_D^{20} - 9.17^\circ$, $[\alpha]_E^{20} - 12.19^\circ$, $[\alpha]_F^{20} - 15.15^\circ$ in ethyl alcoholic solution ($c = 14.059$), and therefore exhibits practically normal rotatory dispersion.

The specific rotation of nopinone has been determined in a variety of solvents (methyl alcohol, chloroform, ethyl iodide, in the pure state, in ether, benzene, *isopentane*, and carbon disulphide). Abnormal rotatory dispersion is observed in each case, the value of the coefficient $[\alpha]_F/[\alpha]_C$ varying from 2.98 for the first-named solvent to 7.95 for the last-named. Further, the specific rotation for any particular ray is greatly dependent on the nature of the solvent, but is very little influenced by change of temperature.

The absorption spectra of nopinol and nopinone have also been investigated. The former only absorbs in the extreme ultra-violet, and gives no characteristic band; the latter absorbs strongly, its

spectrum presenting a diffuse band, the maximum of which is situated towards 3550 rec. A.U. In this case, therefore, the strong and selective absorption corresponds with an abnormal exaltation of the dispersive power.

H. W.

Influence of Pressure on the Absorption of Rays of Very Long Wave-length in Gases. EVA VON BAHR (*Ber. Deut. physikal. Ges.*, 1913, 15, 673—677).—Measurements are recorded of the variation in the absorption of long waves (100—350 μ) in the gases hydrogen chloride, sulphur dioxide, and hydrogen bromide at a series of pressures (20 mm.—760 mm.). The absorption curves are similar to those previously obtained for short wave-lengths (*A.*, 1909, ii, 630; 1910, ii, 914).

J. F. S.

Ultra-red Absorption of Gases. EVA VON BAHR (*Ber. Deut. physikal. Ges.*, 1913, 15, 710—730).—The ultra-red absorption bands of carbon dioxide, carbon monoxide, nitrous oxide, ether vapour, and carbon disulphide have been examined at a series of pressures and temperatures by means of a radiomicrometer using a slit of 0.1 mm. It is shown that the absorption bands at low pressure are not continuous. The discontinuity is less marked as the pressure is increased, so that when the maximum absorption is reached the bands are practically continuous. An increase in the temperature of carbon monoxide brings about a separation of the two maxima of its absorption bands, and also a lateral broadening of the bands. The consequences of the experimental results of the present and previous work is compared with the requirements of the Bjerrum theory of the ultra-red absorption spectra, and generally the agreement between theory and experiment is found to be satisfactory.

J. F. S.

Critical Study of Spectral Series. III. Atomic Weight and its Import in the Constitution of Spectra. WILLIAM MITCHINSON HICKS (*Proc. Roy. Soc.*, 1913, A, 89, 125—127. Compare *A.*, 1912, ii, 512).—It is shown that there is a definite quantity in connexion with each element which is of fundamental importance in the building up of its spectrum. This quantity is proportional to the atomic weight, and if w represents the atomic weight divided by 100, its value is $(90.4725 \pm 0.013)w^2$. This quantity is termed the *oun* (ωv). The evidence for its existence is based on the arc spectra for helium, the elements of the groups I and II, the aluminium sub-group and scandium, also of oxygen, sulphur, and selenium. It is found that the Δ values which give the doublet and triplet separations are all multiples of their respective *ouns*, and that the corresponding quantities, which give the satellite separations in the *D* series, are also multiples of the *oun*. The *F* series also shows satellites depending in a similar way on the *oun*. In a large number of cases, lines are related in such a way that the differences of their denominators are multiples of the *oun*, and that frequently in place of an expected line, which is not observed, another occurs related to it in this manner. It is said

to be collaterally displaced. The paper then deals with the constitution of the *D* and *F* series.

J. F. S.

Ultra-red Absorption Spectra of Some Gases. WILHELM BURMEISTER (*Ber. Deut. physikal. Ges.*, 1913, 15, 589–612).—The absorption spectra of chlorine, bromine, hydrogen, oxygen, hydrogen chloride, hydrogen bromide, cyanogen, hydrogen cyanide, acetylene, carbon monoxide, and carbon dioxide have been determined in the ultra-red region 1μ – 22μ . It is shown that for the elements there are no absorption bands; for the other substances the heads of the absorption bands lie at the following points: hydrogen chloride [3.40, 3.55], hydrogen bromide [3.84, 4.01], cyanogen [3.79, 3.93], 4.65, 13.50, 16.07; hydrogen cyanide, 3.04 [6.95, 7.22], [13.60, 14.33]; acetylene, 2.52, 3.07, 3.77 [7.39, 7.66], [13.50, 13.95]; carbon monoxide, 2.35 [4.60, 4.72]; and carbon dioxide [14.70, 15.05]; the bracketed values represent double bands. The similarity between the spectra of the gases cyanogen and acetylene and the dissimilarity between the spectra of cyanogen and hydrogen cyanide are remarkable.

J. F. S.

Band Spectrum Attributed to Carbon Monosulphide. L. C. MARTIN (*Proc. Roy. Soc.*, 1913, A, 89, 127–132).—A continuation of the work of Strutt and Fowler (*A.*, 1912, ii, 214). It is shown that the arc spectrum of sulphur contains a series of ultra-violet bands extending over the range λ 2436–2837. This band series is also obtained when a spark discharge is passed through carbon disulphide vapour, but not when spark discharges are passed through sulphur vapour, or sulphur chloride vapour. It was observed occasionally in the latter case, but the carbon band λ 2478 was also visible, due to a rubber connexion. The new series of bands, therefore, depends on the presence of both sulphur and carbon, but is unlike the spectra of either element alone. The spectrum of the light produced, when carbon monosulphide is removed from a liquid air cooling mixture, contains the same bands in the ultra-violet.

J. F. S.

New Band Spectrum Associated with Helium. W. E. CURTIS (*Proc. Roy. Soc.*, 1913, A, 89, 146–149. Compare this vol., ii, 539).—A number of bands were observed in the helium spectrum, the chief bands having their heads at λ 6400, 5732, 4649, and 4626. The band 5732 is degraded toward the violet end of the spectrum, and the others in the opposite direction. The author's description of the spectrum is generally the same as that of Goldstein (*loc. cit.*). The spectrum is attributed to helium, although it may possibly be due to hydrogen, because hydrogen has always been present in the tubes.

J. F. S.

Principal and Other Series of Lines in the Hydrogen Spectrum. ALFRED FOWLER (*Zeitsch. wiss. Photochem.*, 1913, 12, 357–371).—The principal and sharp series of hydrogen lines are observed when a strongly condensed discharge is passed through

a mixture of hydrogen and helium. Four members of the principal series and three of the ζ Puppis series were identified. The lines of the principal series have a somewhat smaller wave-length than that calculated by von Rydberg. The wave-length of the first line is $\lambda\lambda 4685\cdot98$ on the Rowland system, which agrees sufficiently well with that observed for the same line in the solar chromosphere and the stars. A second principal series of hydrogen lines was discovered, of which the first line has a wave-length $\lambda\lambda = 3203\cdot30$. The lines in this series converge to the same value as the first principal series. The production of the new lines gives a further proof of the probability that there is no different kind of matter in the stars than that on the earth, and that most of the spectra observed in stars can be reproduced in the laboratory.

J. F. S.

The Red Lithium Line and the Spectroscopic Determination of Atomic Weights. P. ZEEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 155—157).—The lithium red line 6708, previously shown by Zeeman to be a close doublet, has been further examined, and the components shown to be 0.144 Ångström unit apart. It is shown that the regularities found between the differences of the frequencies of the pair lines and the squares of the atomic weights for the elements sodium, potassium, rubidium, and cesium do not hold for lithium.

J. F. S.

New Series in the Spark Spectrum of Magnesium. ALFRED FOWLER (*Proc. Roy. Soc.*, 1913, A, 89, 133—136).—The spark lines were produced when an arc was passed between magnesium electrodes in a vacuum. Five new lines were photographed which are related to the lines $\lambda 4481$, $3106\cdot5$, and $2659\cdot5$. The eight lines make up two series, E_1 and E_2 , and are expressed by the Hicks formulæ:

$E_1(m) = 49775\cdot81 - \{109675/(m + 0\cdot996679 + 0\cdot001552/m^2)\}$
and $E_2(m) = 49776\cdot30 - \{109675/(m + 0\cdot496395 + 0\cdot002884/m^2)\}$.
The two magnesium spark series are similar to the two principal series of hydrogen and run nearly parallel with them. J. F. S.

Additional Triplets and Other Series Lines in the Spectrum of Magnesium. ALFRED FOWLER and W. H. REYNOLDS (*Proc. Roy. Soc.*, 1913, A, 89, 137—145. Compare preceding abstract).—An examination of the arc spectrum of magnesium in a vacuum has shown eight additional triplets, six of which belong to the diffuse and two to the sharp series. Four additional lines belonging to the Rydberg series have been photographed, and it is shown that even a four constant formula does not accurately represent this series. Four strong solar lines of hitherto unknown origin have been identified with lines of the Rydberg series, namely, $\lambda = 4167\cdot44$, $4057\cdot67$, $3986\cdot90$, and $3938\cdot55$. A previously unknown line, $\lambda = 4354\cdot53$, may be united in a series with the known lines $\lambda 5711\cdot31$ and $4730\cdot21$ having the same limit as the Rydberg series.

This series is probably of the sharp type. Several previously known lines have been remeasured, and improved values obtained.

J. F. S.

Series in the Lines of Mercury Spectrum. JOHANNES STARK (*Ann. Physik*, 1913, [iv], 42, 238—240).—Polemical. Reply to Paschen (this vol., ii, 361) with respect to the placing of the lines λ 2536.72 and λ 4078.05 in the same series.

J. F. S.

Reflection Spectra of Compounds of Neodymium. PAUL JOYE (*Arch. Sci. phys. nat.*, 1913, [iv], 36, 41—58, 113—138).—The reflexion spectra of a number of neodymium compounds have been photographed and measured. The substances measured include three hydrates: $\text{Nd}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, $2\text{Nd}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, $\text{Nd}_2\text{O}_3 \cdot \text{H}_2\text{O}$, the oxide, sulphide, sulphate, chloride, bromide, carbonate, oxalate, and nitrate. The absorption spectra of solutions of the nitrate and chloride are also described. A full list of the absorption bands measured is given, and the relationships between the various bands are discussed.

J. F. S.

The Radiations from Nitrogen. MAURICE HAMY (*Compt. rend.*, 1913, 157, 253—257).—An extension of the work of Fabry and Buisson (compare *J. Physique*, 1912, June) to the spectra of bands, and in particular to those which do not appear to be sensitive to a magnetic field, the example chosen being those obtained from nitrogen and lying between λ 440 and λ 410. The method of measurement has already been described (*ibid.*, 1906, 189). The results show that the optical width of the radiations composing the refrangible bands of the positive spectrum of nitrogen obey the same law as that of the rays of the line spectra, a law which is independent of the theories relying on the generation of the luminous vibrations.

W. G.

Spectroscopic Investigations in Connexion with the Active Modification of Nitrogen. III. Spectra Developed by the Tetrachlorides of Silicon and Titanium. WILFRED JEVONS (*Proc. Roy. Soc.*, 1913, A, 89, 187—193. Compare Fowler and Strutt, A., 1911, ii, 482, 678; 1912, ii, 214).—The author has introduced the vapours of silicon tetrachloride and titanium tetrachloride into the after-glow of active nitrogen, and examined the spectra. In the former case a number of bands between λ 3800 and 4950 have been observed; these are attributed to a nitride of silicon, whilst in the latter case there is no evidence of a nitride of titanium. The new silicon nitride bands degrade towards the red, and show intense minima near the heads, corresponding with the modifications of the cyanogen after-glow bands.

J. F. S.

Arc and Spark Lines of Oxygen in Canal Rays. JOHANNES STARK, G. WENDT, and H. KIRSCHBAUM (*Physikal. Zeitsch.*, 1913, 14, 770—779).—The spectra of oxygen in helium and oxygen canal rays have been measured. It is shown that increasing the cathode

potential fall from 3200 volts to 15,000 volts causes an increase in the intensity of all lines of oxygen in oxygen canal rays. It is also shown that there are two series of oxygen spark lines characterised as sharp and unsharp lines. Two arc spectra are also observed, and it is shown that the carriers of the lines of the first spectrum are positive univalent oxygen molecules.

J. F. S.

Series Lines of Oxygen in Canal Rays. JOHANNES STARK (*Physikal. Zeitsch.*, 1913, 14, 779—780).—Polemical. A further criticism of Wilsar's work (this vol., ii, 172, 359; see also Stark, this vol., ii, 172).

J. F. S.

Band Spectrum of Silicon Tetrafluoride. C. PORLEZZA (*Gazzetta*, 1913, 43, ii, 124—128).—The author has re-investigated this spectrum, already measured by Dufour, and the new measurements are recorded in the present paper. Three new lines (wave-lengths 4616·57, 4609·61, 4605·25) have been observed. The measurements refer to the spectrum of undecomposed silicon tetrafluoride which is obtained when no condenser is employed. If the intensity of the discharge is increased by the use of condensers, however, a line spectrum is obtained due to silicon and fluorine; this has already been described (*A.*, 1912, ii, 876).

R. V. S.

The Origin of Some Groups of Bands in the Spark Spectrum of Salts of Strontium. S. PIENKOWSKI (*Bull. Acad. Roy. Belg.*, 1913, 607—613).—The spark spectrum of strontium chloride is measured, both in air and in hydrogen. The spark is produced by a coil fed with a current of 20—25 amperes at 110 volts, using a Wehnelt interrupter making 350—400 breaks per second. The spark in this way is 0·7 cm. long. It is shown that the bands at λ 4583, 4565, 4545, 4524, 4421, 4401, 4340, 4305, and 4281 are due to the oxide.

J. F. S.

Arc Spectrum of Tellurium. HORACE SCUDDER UHLER and R. A. PATTERSON (*Amer. J. Sci.*, 1913, [iv], 36, 135—140).—The arc spectrum of pure tellurium has been determined, using gratings of 1 metre radius of curvature and 18159 lines in 4·6 cm. and 6·55 metres radius of curvature and 5905 lines per cm. Fifteen lines have been measured lying between 3175·130 Å and 2081·8 Å, measured on the international scale. The line 3175·130 is shown to be distinct from the tin line 3175·044, and the line 2769·653 distinct from the antimony line 2769·939 by mixing tellurium with tin and antimony respectively, and photographing the spectrum of the mixtures when the two lines in each case are obtained. The arc was produced in an atmosphere of carbon dioxide between tellurium electrodes for the earlier measurements, and later by placing pieces of tellurium on the lower carbon pole of a carbon arc.

J. F. S.

Absorption Spectrum of Aqueous Vapour. EVA VON BARR (*Ber. Deut. Physikal. Ges.*, 1913, 15, 731—737).—The bands at

5.9μ and 6.5μ have been re-measured, and from the measurements it is shown that both parts of the bands are made up of a number of separate lines. The rotation wave-lengths calculated from these lines coincide with those found by Rubens in the region of the residual rays. It is shown that the bands 5.9μ and 6.5μ are probably to be regarded as Bjerrum double bands. J. F. S.

Inflexion Point in the Absorption Boundary Curve; Long Wave-length Absorption Bands of Acetone. JOHANNES STARK (*Physikal. Zeitsch.*, 1913, 14, 845—847).—The conditions under which a point of inflexion can occur in an absorption spectrum curve are considered, and it is shown that a point of inflexion in one branch of a band of an absorption boundary curve or an absorption index-wave-length curve is an indication of the presence of a less intense band in the same wave-length region as the first band. The absorption curve of acetone is then considered, and since this shows a point of inflexion (Bielecki and Henri, *Physikal. Zeitsch.*, 1913, 14, 516; see this vol., ii, 363), it is concluded that acetone, in addition to the known short wave-length bands, has a still less intensive long wave-length ultra-violet band above λ 330 $\mu\mu$. J. F. S.

The Presence of Absorption Bands in the Ultra-violet Spectrum of Some Abnormal Alcohols of the Fatty Series. GUSTAVE MASSOL and A. FAUCON (*Compt. rend.*, 1913, 157, 386—388).—A study of the ultra-violet absorption spectra of some normal, primary, secondary, and tertiary alcohols, and also of three abnormal primary alcohols. All the alcohols exhibit a progressive absorption for radiations of short wave-length. The secondary alcohols are slightly more transparent than the normal primary alcohols with the same carbon content, whilst the tertiary alcohols are markedly more transparent. The three abnormal primary alcohols studied showed two absorption bands, the one from $\lambda=2500$ to 2700, and the other from λ 3060 to 3150. These bands are special to the alcohols, and cannot be found either with the fundamental hydrocarbon, with the other alcohols, or with the corresponding alkyl haloids. The corresponding aldehydes present one single broad band coming between the two bands of the alcohols. W. G.

Quantitative Study of the Absorption of the Ultra-violet Rays by Some Acids of the Ethylene Series. JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1913, 157, 372—375).—The authors have determined the absolute values of the absorption of the ultra-violet rays for a number of acids containing an ethylene linking, and from a comparison with the corresponding saturated acids have determined the influence of such a linking, and also of its position with respect to the carboxyl group.

The ethylene linking in acids produces a rise in the absorption, the increase being greater the nearer the linking is to the carboxyl group. In the case of geometrical stereoisomerides, the *cis*-isomeride

absorbs less than the *trans*. The influence of the ethylene linking cannot be expressed in the form of an additive constant, but as a factor according to the following law: For a substance of formula $ABC \dots$, the molecular constant of absorption ϵ is equal to a product, $\epsilon = (abc \dots) (\alpha\beta \dots)$, where a, b, c, \dots are factors corresponding with the different molecular groups A, B, C \dots and α, β, \dots are factors which indicate the effect of the linking, configuration, and reciprocal positions of the groups. These results are borne out by a similar study of the alcohols. W. G.

Absorption Spectra of the Red Dyes Sanctioned for Use in Confectionary. GUSTAVE MASSOL and A. FAUCON (*Bull. Soc. chim.*, 1913, [iv], 13, 803—807. Compare this vol., ii, 264, 542, 742).—The method of investigation used is that previously described. The spectra of eight dyes have been studied. Those derived from naphthaleneazonaphthol (Bordeaux B., crystal-ponceau, Bordeaux S, new coccine, fast red) and those from xyleneazonaphthol (ponceau RR, scarlet R) show similar spectra, both in the visible and invisible portions, yielding a broad band which extends from the yellow to the violet for small thicknesses, and covers the whole of the latter in the case of layers of 30 to 50 mm. They are very absorbent for the ultra-violet.

Acid magenta, on the other hand, is very transparent to the violet rays, and gives a band covering the green and blue which, for short layers (8 to 18 mm.), separates into two distinct bands. Unlike the other reds, acid magenta is very transparent to the invisible rays of wave-length greater than 320—330; for layers of 10 mm. the spectra show a sharp alteration in the absorption between $\lambda = 270$ and $\lambda = 300$.

A short summary of the results of this series of investigations is also given. H. W.

Emission of Series Lines by Canal Rays. JOHANNES STARR (*Ann. Physik*, 1913, [iv], 42, 163—180).—The intensity of the series lines is brought about by the collision of canal ray particles with the non-luminous atoms, the canal ray particle passing through their periphery and bringing about an ionisation. The relationship of the intensity of the higher valence lines to that of the univalent lines increases with increasing velocity of the light of the canal rays. Helium-canal rays tend to produce low valence lines of other elements. It is shown to be probable that the collision of heavy canal-ray particles on aluminium atoms occasions changes of both light energy and kinetic energy. The canal rays of heavy elements allow helium atoms, which lay in their path, to pass through their outside layer without any marked change in their kinetic energy. J. F. S.

Fluorescence of the Elements of the Sixth Group of the Periodic System. Sulphur, Selenium, and Tellurium Vapours. WALTER STREUBING (*Physikal. Zeitsch.*, 1913, 14, 887—893).—The four elements of the sixth group of the periodic system show a

marked fluorescence in the gaseous condition. The fluorescence moves from regions of short wave-length to regions of longer wave-length with increase of atomic weight. For oxygen, fluorescence is exhibited below λ 2000 Å.; for sulphur, between λ 2500 Å. and λ 3200 Å.; for selenium, from λ 3000 Å. into the visible region, and for tellurium in the most refrangible part of the visible region. A definite density and temperature is necessary for production of fluorescence; for example, in the case of sulphur vapour a temperature of 400–500° is necessary. The fluorescence spectra are discontinuous, and show more or less feeble groups of lines which have the appearance of bands. The fluorescence is greatly weakened by mixing the vapours with other gases or vapours.

J. F. S.

Phosphorescence of Mercury Vapour after Removal of the Exciting Light. F. S. PHILLIPS (*Proc. Roy. Soc.*, 1913, A, 89, 39–44).—The phosphorescence of mercury vapour has been observed by directing a beam of light $\lambda = 2536$ from a water-cooled quartz mercury lamp on to an exhausted quartz tube, in which a stream of mercury vapour is produced by distilling mercury from one limb into the other. The mercury fluoresces at low pressures, and persists after the vapour has passed the exciting beam of light. The fluorescence of the vapours of iodine, anthracene, and retene was examined by the same method, but with negative results.

J. F. S.

Rotatory Power of Some Organic Complexes of Molybdic Acid. ARRIGO MAZZUCHELLI, C. RANUCCI and A. SABATINI (*Gazzetta*, 1913, 43, ii, 26–59. Compare Mazzucchelli, A., 1911, i, 10; Mazzucchelli and Borghi, A., 1911, i, 11).—From the authors' measurements with solutions of mixtures of tartaric and molybdic acids, as well as from those of Rosenheim and Itzig (A., 1900, i, 135, 272), it appears that the rotatory power of the organic acid in presence of any given quantity of molybdic acid is not absolutely fixed, but varies within limits which exceed those of experimental error. It is suggested that the solutions may present a case of false equilibrium.

The rotatory power of solutions containing molybdic acid, tartaric acid, and a third indifferent, inactive acid (acetic acid, hydrochloric acid), is not seriously affected by the presence of the last-named, so that polarimetric measurements may be used to determine the partition of molybdic acid in a solution between tartaric acid and any other acid capable of forming molybdic complexes but inactive.

The difference between the white and yellow molybdic acids in regard to tartaric acid, confirmed in the previous paper (*loc. cit.*), has since been found not to exist; where the differences are not accidental they may be referred to the methyl alcohol present. The same similarity of behaviour towards tartaric acid was also observed in the case of molybdic acid from other sources (by acidification of ammonium paramolybdate "Merck," acid ammonium

molybdate, $3(\text{NH}_4)_2\text{O} \cdot 8\text{MoO}_3 \cdot 4\text{H}_2\text{O}$, and potassium trimolybdate, respectively).

Further measurements of the rotatory power of solutions containing tartaric acid and various molybdates of sodium and potassium show that the rotatory power depends only on the relative proportions of the constituents, and not on the order of addition or on the nature of the molybdate added (compare *loc. cit.*). Hence if a solution of an alkaline tartrate does not dissolve more than an equimolecular quantity of molybdic acid, this is due only to the slowness of the heterogeneous reaction.

Towards malic acid the white and yellow molybdic acids behave alike; in both cases indications of the existence of two compounds, $\text{C}_4\text{H}_6\text{O}_5 \cdot \text{MoO}_3$ and $\text{C}_4\text{H}_6\text{O}_5 \cdot 2\text{MoO}_3$, are found.

The white and yellow molybdic acids behave similarly towards quinic acid. The rotatory power of the solutions is altered by addition of ethyl alcohol, as well as by that of methyl alcohol, and the rotatory power is also considerably affected by changes of concentration.

Measurements of the rotatory power of mixtures of molybdic and tartaric acids to which hydrogen peroxide had been added showed the existence of two peracids, $\text{C}_4\text{H}_6\text{O}_6 \cdot \text{MoO}_3 \cdot \text{H}_2\text{O}_2$ and $\text{C}_4\text{H}_6\text{O}_6 \cdot 2\text{MoO}_3 \cdot \text{H}_2\text{O}_2$. There may be also compounds in the proportions 1:2:2, 1:3:2, and 1:3:3, or the values observed at these concentrations may be due to dissociation of the compound 1:2:1. In any case, compounds other than these do not exist (compare Mazzucchelli and Borghi, *loc. cit.*). When the ratio $\text{MoO}_3:\text{H}_2\text{O}_2$ exceeds 1:2, the rotatory power diminishes considerably.

The rotatory power of mixtures of malic acid, molybdic acid, and hydrogen peroxide does not change appreciably on keeping; the values obtained are not much influenced by temperature, but vary considerably with the total concentration of the solution. The addition of the peroxide diminishes the rotatory power, which becomes negative when the concentration reaches $\text{MoO}_3 \cdot 2\text{H}_2\text{O}_2$.

The addition of peroxide to solutions of quinic acid and molybdic acid also causes a diminution of rotatory power. R. V. S.

The Photochemical Equivalent. EDWARD C. C. BALY (*Physikal. Zeitsch.*, 1913, 14, 893—896).—The theory of electric fields surrounding molecules is developed by the author, and experimental evidence is advanced to show the addition of a molecule of an acid to a base to form an additive compound before the formation of a salt takes place. These actions are studied spectroscopically in the case of *p*-aminobenzaldehyde and hydrochloric acid, and in the sulphonation of quinol dimethyl ether (compare Baly and Rice, T. 1912, 101, 1475). It is shown that experiments of Henri and Wurmser (this vol., ii, 369) give values for the quantity of light absorbed by the photochemical reactions they have observed, which are too small, and it is suggested in opposition to the above authors that a portion of the necessary energy is derived from the solvent. J. F. S.

Theory of Photochemical Reaction Velocity. MAX BODENSTEIN (*Ber. Deut. physikal. Ges.*, 1913, 15, 690—704).—A theoretical paper in which an hypothesis of the mechanism of photochemical reactions is put forward and examined in connexion with a large number of published photochemical changes. It is assumed at the outset that every photochemical reaction is a photoelectrical change in which a molecule is divided, with absorption of light energy, into an electron and a positive residue with a free valency. Both parts are then capable of reaction; the positive residues react either with one another or with other molecules, the electrons by combining with other molecules and rendering them capable of reaction. This leads to reactions of two kinds, primary light reactions occurring between the positive residue and other molecules, and secondary light reactions between molecules which have been rendered active by combining with an electron. Both types of reactions are developed in the paper.

J. F. S.

Influence of Oxygen on the Selective Photo-effect of Potassium. ROBERT POHL and P. FRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1913, 15, 625—636).—When potassium is brought into contact with oxygen at low pressure a dark-coloured surface layer is formed, which consists of a solution of colloidal potassium in a compound of potassium and oxygen. This mixture is strongly photoelectrically active, so much so that in the violet end of the spectrum a yield of 240×10^{-4} coulomb per light calorie is observed. The maximum of this selective activity is displaced 7% from that of pure potassium in the direction of smaller wave-length, from $\lambda = 436 \mu\mu$ to $\lambda = 405 \mu\mu$. At the same time, there is a large increase in the electron emission below $\lambda = 280 \mu\mu$, which is to be regarded as the normal photo-effect of potassium oxide.

J. F. S.

The Rôle of Uranium Salts as Photochemical Catalysts. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, 157, 333—335).—A continuation of experiments on the behaviour of uranium salts as photochemical catalysts (compare A., 1911, ii, 170). Apart from salts of uranium, neither the fluorescent nor radioactive substances, experimented with, accelerated photochemical reactions. The accelerating influence of the uranium salts is limited to a special class of reactions, namely, the decomposition of open-chain acids, especially dibasic or complex acids. These are reactions which occur spontaneously in ultra-violet light, and, under the influence of the catalyst, they take place in visible light. The catalyst thus lowers the vibration frequency of the photochemical reaction, in the same way as an ordinary catalyst lowers the temperature of a chemical reaction.

W. G.

Negative Photocatalysis of Hydrogen Peroxide. VICTOR HENRI and RENÉ WUMMER (*Compt. rend.*, 1913, 157, 284—287).—The addition of traces of numerous different substances to hydrogen peroxide renders it stable towards ultra-violet rays, alkalis being more active than acids in this respect. The authors suggest that,

in many of the cases of catalysis by ferments and colloidal metals, the action of poisons is on the substances undergoing transformation, and not on the catalyst itself. Further, that the action of certain ferments is quite comparable to that of the ultra-violet rays.

W. G.

Absorption of Ultra-violet Rays by Some Mineral Colouring Matters in Aqueous Solution. GUSTAVE MASSOL and A. FAUCON (*Compt. rend.*, 1913, 157, 332—333. Compare this vol., ii, 742).—A study of the absorption of the ultra-violet rays by aqueous solutions of such substances as potassium ferrocyanide, gold chloride, copper sulphate, &c. These colouring matters exhibit various powers of absorbing ultra-violet rays, and are far less powerful than synthetic organic dyes, although qualitatively the absorption is of the same order, and in the case of band spectra, broad absorption bands occur in the same regions of the spectrum, these depending on the colour, and not on the chemical constitution of the substance.

W. G.

Rays of Positive Electricity. SIR JOSEPH J. THOMSON (*Proc. Roy. Soc.*, 1913, A, 89, 1—20).—The Bakerian Lecture. The properties of positive rays are considered, together with the author's method of examination by subjecting them to electric and magnetic fields. The use of this method of investigation is considered, and its application to the analysis of the gases in excited tubes. The author shows that the heavier constituents of the atmosphere probably contain a gas of atomic weight about 22, and that neon is probably a mixture of two gases of atomic weights respectively about 20 and 22. The production of a gas of atomic weight 3 (X_3) is considered; this gas is produced along with helium when metals and salts are bombarded by cathode rays, and the production of the gas is not diminished when the salts are dissolved in water or alcohol, evaporated to dryness, and then bombarded. The possible nature of the gas X_3 is considered. It is shown that it may be stored over mercury for weeks; it may be heated in a quartz tube to a red heat without change; sparking with oxygen and heating with phosphorus have no action on the gas, and it does not combine when heated with sodium vapour. On the other hand, it combines with mercury vapour when an electric discharge is sent through the mixture, and it combines to some extent with red hot copper. In a note added to the paper the author shows that there is a genuine production of helium and X_3 apart from liberation of absorbed gas when salts of the alkali and alkaline-earth metals are bombarded. This is regarded as remarkable, since potassium has been already shown to be radioactive. In the case of potassium iodide evidence was obtained of the existence of a gas of atomic weight 35, which represents the difference between the atomic weights of potassium and helium.

J. F. S.

Collisions Between Gas Molecules and Slow Moving Electrons. II. J. FRANCK and GUSTAVE HERTZ (*Ber. Deut. physikal. Ges.*, 1913, 15, 613—620. Compare this vol., ii, 548).—The conclusion

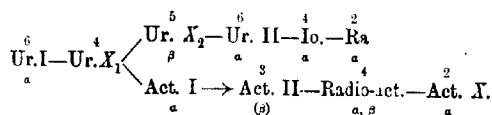
GENERAL AND PHYSICAL CHEMISTRY.

arrived at in Part I., namely, that the collisions between electrons and gas molecules are more elastic the smaller the electron affinity of the gas molecule, is confirmed. It is shown for the gases helium, hydrogen, and oxygen that the energy necessary for ionisation is not obtained by the electrons on a single free path. In the case of helium the ionisation energy can be obtained during any number of collisions; in the case of hydrogen the number is limited by the energy loss at the collision, and in oxygen it is still smaller, since the strong electronegative character of oxygen conditions markedly inelastic collisions between electrons and molecules. J. F. S.

Radium Content of Certain Varieties of Mud. ERNST HENDRIK BUCHNER (*Chem. Weekblad*, 1913, 10, 748-751).—The presence of radium as sulphate has been detected in samples of blue and brown mud from Rockanje. A. J. W.

Determination of the Strength of Radium Preparations. WILLEM P. JORISSEN (*Chem. Weekblad*, 1913, 10, 710-711).—A description of an application of Rutherford's method to the valuation of a radium preparation accidentally contaminated with foreign material. A. J. W.

Complex Nature of Radio-actinium and the Position of Actinium in the Periodic System. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1913, 14, 752-758).—By means of determinations on the change of the α - and β -ray activity of actinium which had been freed from radio-actinium-I the authors are unable to find any evidence of the existence of an intermediate product between radioactinium and actinium-X. Such a substance, radio-actinium-2, is stated to exist by Chadwick and Russell (this vol., ii, 274), and to have a half-life of thirteen hours. The position of actinium in the periodic system and in uranium series is discussed. It is held that actinium is trivalent, and is derived from a quinquevalent parent substance which emits α -rays. The following scheme is put forward to indicate the position of actinium in the uranium family:



J. F. S.

Uranium-X₂. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1913, 14, 758-759).—A method of isolation of uranium-X₂ is given. Uranium-X is separated from uranium by means of ammonium carbonate. The uranium-X is dissolved in fairly strong acid, and filtered through a filter paper on which tantalum pentoxide had previously been filtered. In this way the uranium-X₂ is held back and freed from all but about 1% of uranium-X₁. From measurements of the activity of the tantalum pentoxide the half-

life of uranium- X_2 is determined as 1.17 minutes. Uranium- X_2 is shown to have properties homologous to those of tantalum, and its penetrating β -rays are identical with those of the undivided uranium- X . There is no evidence to show whether uranium- X_2 is the origin of the slow β -rays found in the original uranium- X . It is held that uranium- X_2 is a direct product of uranium- X_1 .

J. F. S.

Liquid Helium. II. The Electrical Resistance of Pure Metals, etc. VII. The Potential Difference Necessary for the Electric Current Through Mercury Below $4.19^\circ K$. H. KAMMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 113—124. Compare this vol., ii, 748).—A theoretical paper, in which the local heating and consequent resistance changes of a thread of mercury at temperatures below $4.19^\circ K$ are discussed. It is shown that a different crystalline form of the solid mercury is not sufficient to account for the increased resistance at $3.65^\circ K$. These superconducting points cannot be accounted for on the Wiedemann and Franz or the Lorenz relationships. An electronic theory is put forward and discussed.

J. F. S.

Electrical Conductivity of Concentrated Aqueous Solutions. ALEXANDER N. SACHANOV (*Zeitsch. Elektrochem.*, 1913, 19, 588—589).—The conductivities of concentrated solutions of silver nitrate, lithium chloride, and lithium chlorate have been measured. The viscosities of the same solutions have also been determined, and the conductivity values corrected for the change in viscosity by means of the formula $L = \lambda(\eta/\eta_0)^m$, in which L is the corrected conductivity, λ the measured conductivity, η_0 the viscosity of the solvent, and η that of the solution; m is a constant with a value approximating to unity. It is shown in this way that the conductivity of concentrated solutions is abnormal, inasmuch as the molecular conductivity increases with increasing concentration. The values of Kohlrausch for ammonium nitrate, potassium bromide, and potassium iodide have been treated in the same way, and these salts are also shown to be abnormal.

J. F. S.

Electrical Conductivity of Alloys of Copper and Tin. NIKOLAI A. PUSCHIN and A. V. BASKOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 746—752).—The curves showing the variation of (1) the specific resistance, and (2) its temperature-coefficient with the composition of copper-tin alloys consist each of six branches, corresponding with the following ranges of composition (atom. % of tin): 0—7, 7—20, 20—25, 25—40, 40—50, 50—100. The resistance curve shows a minimum and the temperature-coefficient curve a maximum at 25 atom. % of tin, the magnitude of the coefficient being similar to the values obtained for pure metals; these results indicate the existence of a definite chemical compound, Cu_3Sn , and are in agreement with those of thermal analysis, etc.

The low value of the temperature-coefficient corresponding with

the composition Cu_3Sn indicates the formation, not of a definite compound, but of a solid solution.

Whilst the addition of tin to copper causes a very rapid increase in the resistance, copper produces but little change in the resistance of tin.

T. H. P.

Experimental Determination of a Dropping Electrode Potential in Water Alcohol Mixtures. H. KRUMREICH (*Zeitsch. Elektrochem.*, 1913, 19, 622—636).—The author has determined the potential of a dropping electrode in aqueous and aqueous-alcoholic solutions of potassium nitrate. The values obtained are compared with those deduced from the electro-capillarity curve for the same solutions, and it is shown that they are generally in good agreement. Measurements were also made to show the dependence of the potential on the mercurous ion concentration in the same solutions. It is shown in this connexion that the agreement is much better in the aqueous-alcoholic solutions than in the aqueous solutions. Very full details are given of the apparatus employed and of the precautions which must be observed to obtain reproducible and correct measurements.

J. F. S.

Influence of Pressure on the E.M.F. of the Lead Accumulator. ERNST COHEN and G. DE BRUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 161—164).—The paper deals with the experimental determination of the relationship between the influence of pressure on the E.M.F. of a galvanic cell and the volume changes which occur when the quantity of electricity $d\epsilon$ passes through it. This is represented by the equation:

$$-(dE/dp)_{T,p} = (dv/d\epsilon)_{T,p}$$

where E is the E.M.F. of the cell, p the pressure, and dv the change of volume. This change can be calculated if the specific volume of the system before and after the passage of the current $d\epsilon$ is known, or it can be determined experimentally. The authors fitted two perforated lead electrodes in a dilatometer filled with dilute sulphuric acid, and after forming the electrodes the apparatus was placed in series with two silver voltmeters, a milliammeter, and a resistance. The temperature was kept at $15.00^\circ \pm 0.005$, and a current passed for twenty hours. The silver deposited was weighed, and the volume change determined from a graduated capillary tube, into which the liquid of the dilatometer was forced. In this way from three experiments it is found that the volume increase is 3.67 c.c. per gram-equivalent. Calculating from the change in the specific volume the value 3.54 c.c. was obtained.

J. F. S.

Tantalum as a Cathode Material. G. OSTERHELD (*Zeitsch. Elektrochem.*, 1913, 19, 585—587).—Experiments have been made with tantalum with the object of testing its suitability as a cathode. It is shown that in a 2N-sulphuric acid solution the overvoltage is 1.14 volts. It is also shown that as a reducing electrode in the case of benzophenone, caffeine, and nitrobenzene, it gives exceedingly poor yields. It is also shown to absorb hydrogen

and at the same time to lose its elastic properties and become crystalline and brittle. A series of discharge potential measurements made in 2*N*-sulphuric acid are recorded. It is thus shown that tantalum can have but a very restricted use as a cathode material.

J. F. S.

Electrolytic Valve Action of Metals. W. WINTER (*Physikal. Zeitsch.*, 1913, 14, 823—828).—It has been shown by Schultze (A., 1907, ii, 842; 1908, ii, 350, 560, 658; 1909, ii, 371; 1911, ii, 365; 1912, ii, 126, 529) that many metals in addition to aluminium exhibit a valve action on the alternating current. It has been suggested that the valve action is brought about by an active layer on the electrode, which of itself is non-conducting. The current is conveyed by a series of pores filled with electrolyte, except in the immediate neighbourhood of the electrode, where a thin gas layer exists, and consequently the current can only be conveyed in the direction of the metal. The author has tested this explanation by binding sheets of several metals on the outside of a porous pot filled with an electrolyte in which a carbon electrode was placed. It is shown that in potassium hydroxide solution under these conditions the metals magnesium, aluminium, zinc, cadmium, iron, cobalt, nickel, lead, tin, antimony, bismuth, copper, silver, platinum, gold, and chromium show a strong anodic valve action, whilst in dilute sulphuric acid all except the last three show the same action. Hydrochloric acid and nitric acid show a very slight valve action in some cases, but generally there is no valve action under the experimental conditions. An amalgamated gold electrode in dilute sulphuric acid showed the valve action. The cause of the action is considered, and it is shown that electrolytic and Wehnelt effects do not explain the phenomenon. It is considered likely that the metals under investigation form layers which in ordinary circumstances would be dissolved and removed from the surface of the electrode.

J. F. S.

Partition of Electrolytes between Water and a Second Solvent. NILRATAN DHAR and ASWINI KUMAR DATTA (*Zeitsch. Elektrochem.*, 1913, 19, 583—585).—The authors have determined the partition of lithium chloride and cadmium iodide between water and amyl alcohol, and the latter salt between ether and water. The object of the investigation was to determine from the results the degree of dissociation of the dissolved salts. The results, however, show that the method is unsuitable for such determinations; the values obtained in this way differ as much as 58% from those obtained from conductivity determinations.

J. F. S.

The Dissociation of Good Electrolytes and the Law of Mass Action. PAUL TH. MÜLLER and R. ROMANN (*Compt. rend.*, 1913, 157, 400—403. Compare this vol., ii, 679).—A theoretical discussion of results obtained and previously given (compare *loc. cit.*) in support of their view that the results must be due to the fact that the base and acid generators of a good electrolyte themselves

follow the law of mass action and possess ions the hydration of which is constant at dilutions above 1 gram-molecule in 100 litres of water.

W. G.

Formation of Sodium Hypochlorite with Cooled Anodes.

PAUL H. PRAUSNITZ (*Zeitsch. Elektrochem.*, 1913, 19, 676—680).—A cooled platinum anode has been used in the preparation of hypochlorite solutions; it is shown that in a 5*N*-sodium chloride solution at 20° electrolyte temperature, an improved hypochlorite concentration can be obtained if a somewhat higher anode current density (C_A) is employed. Without cooling, the highest value obtainable is 41.6 grams of bleaching chlorine per litre, whilst if the anode temperature is maintained at 15° the value rises to 90 grams per litre and at 3—4° to 100 grams per litre, C_A in the above cases being 1.25 amperes per sq. cm. The current efficiency at the beginning of the process is high, but afterwards falls off somewhat. Gradual raising of the temperature of the water flowing through the anode showed that with the electrolyte at 20—25° and $C_A = 1.25$ amperes per sq. cm., the temperature of the anode must have been about 40°. Cooling the anode to 20° and raising the temperature of the electrolyte (5*N*-NaCl) to 48° gave a maximum yield of 70 grams of bleaching chlorine per litre with a terminal potential reduced 20%, and a current efficiency of over 50%. In a *N*-sodium chloride solution, cooling the anode is without influence. At smaller values of C_A , for example, 0.47 ampere per sq. cm. in 5*N*-sodium chloride solution and with the anode at 12°, an increase in concentration from 39.7 to 49.1 grams of bleaching chlorine per litre is obtained. Platinising of the anode and cooling gives at $C_A = 0.47$ ampere per sq. cm. an increase of from 47 to 60 grams of bleaching chlorine per litre. The current efficiency is in this case as high as in the case where Turkey-red oil and chromate are used with platinised electrodes (Prausnitz, this vol., ii, 49).

J. F. S.

Departures From the Curie Law in Connexion with the Zero Energy Point. E. OOSTERHUIS (*Physikal. Zeitsch.*, 1913, 14, 862—866).—Instances are quoted to show that a large number of substances do not obey the Curie law, $\chi T = \text{constant}$, for at low temperatures the value decreases. This divergence is discussed, and it is shown that the three types of divergence from the Curie law can be united under the theory of a zero rotational energy point. The zero energy point is shown to be a reality by the course of the specific heat of hydrogen at low temperatures (Einstein and Stern). The theory of free electrons in metals is explained by the theory of quanta, using the conception of a zero energy point.

J. F. S.

Present State of the Temperature Scale. GEORGE KIMBALL BURGESS (*J. Chim. phys.*, 1913, 11, 529—542).—Some uncertainty attaches to the corrections to be applied to the readings of the gas thermometer to convert them to absolute thermodynamic tempera-

tures, but helium and hydrogen between -50° and $+75^{\circ}$ depart so little from perfect gases that the correction in constant volume thermometers is less than 0.001° .

The usual secondary standards are mercury in glass or quartz up to 755° and toluene or pentane in glass for low temperatures. The readings depend on the kind of glass and its previous history. The platinum resistance thermometer from 200° to 1000° is very exact, and the constant in Callendar's formula for the particular piece of platinum may be determined by measurements at 0° , 100° , and 32.383° (transition point of sodium sulphate), or $444.6^{\circ} \pm 0.1^{\circ}$ (boiling point of sulphur). The error at 1100° is less than 2° . With the platinum resistance thermometer 0.0001° is appreciable at $+25^{\circ}$.

The platinum-rhodioplatinum thermo-junction is of inferior accuracy, necessitating rather large corrections, and being subject to unknown errors due to lack of homogeneity in the wires.

The author gives a list of twenty-four boiling, fusing, and transformation points ranging from -252.7° to $+3000^{\circ}$, which are available as fixed points in thermometry, noting the degree of approximation of each.

The International Bureau of Weights and Measures has now a scale of temperatures from 0° to $+100^{\circ}$ with a maximum error of 0.002° . Outside of these limits there is no general agreement as to the basis of temperature measurements. Between $+450^{\circ}$ and $+1550^{\circ}$ the nitrogen thermometer is commonly used, and above 1550° radiation pyrometers, the constants of which have been determined at lower temperatures. It should be possible to establish an international scale up to 1000° .
R. J. C.

An Easy Method of Obtaining Temperatures as Low as -211° by the Use of Liquid Nitrogen. GEORGES CLAUDE (*Compt. rend.*, 1913, 157, 277—279, 397).—By rapidly bubbling hydrogen, previously passed through a copper spiral immersed in liquid nitrogen, through liquid nitrogen in a silvered vacuum vessel, the temperature rapidly falls. In one experiment it reached -200° after two minutes, -206° after six minutes, and -210° after twelve minutes. The hydrogen should pass at the rate of 20—25 litres per minute.

In the second paper the author points out that Dewar has already described this process in 1904.
W. G.

New Designs for Specific Heat Apparatus. ARDEN R. JOHNSON and BERNARD W. HAMMER (*J. Amer. Chem. Soc.*, 1913, 35, 945—948).—The principle of the one apparatus is that a definite amount of heat is supplied to the liquid in the calorimeter by immersing an electric lamp in it and passing the current for a definite time. Using water in the one case, and the liquid under investigation in the other, and making appropriate corrections for radiation, the specific heat of the liquid under investigation is readily determined. The determination may also be made by comparing the amounts of electrical energy necessary to raise

given weights of water and the other liquid through a definite range of temperature. For this apparatus a very constant voltage is required.

In another apparatus a variable voltage may be used. An electric light bulb is fastened into a copper vessel containing 100 grams of water. The whole is raised to a definite temperature by means of the lamp, and is then used as the hot body for immersion in the liquid in the calorimeter.

T. S. P.

Calculation of Specific Heats from Elasticity Constants. ARNOLD EUCKEN (*Ber. Deut. physikal. Ges.*, 1913, 15, 571—577).—A theoretical paper in which the calculation of specific heats by means of the formulæ of Born and Kármán and Debye is discussed. It is shown that probably the theoretically deduced relationship exists between elasticity and heat content for crystals at low temperatures.

J. F. S.

Experimental Examination of the T^3 Law for the Course of the Specific Heat of Solid Substances at Low Temperatures.

ARNOLD EUCKEN and FRÉDÉRIC SCHWERS (*Ber. Deut. physikal. Ges.*, 1913, 15, 578—588).—The specific heats of lead, fluorspar, and pyrites have been determined at a series of low temperatures with the object of confirming Debye's law (*A.*, 1912, ii, 1134). The determinations were carried out by an electrical method and with the least possible weight of apparatus, in order to reduce the quantity of heat required to raise the temperature of the calorimeter and its contents. The measurements were made for lead between 15.95° and 92.0° abs., fluorspar 17.5° and 86.0° abs., and pyrites 21.7° and 84.0° abs. At these temperatures the molecular heat of fluorspar and pyrites varies proportionally to the cube of the absolute temperature, the values varying between 0.07 cal. and 1.0 cal. Consequently, within this region the theory of Debye, which was supposed to hold for monatomic substances only, is applicable to regular polyatomic crystals. The molecular heat of fluorspar follows the Debye theory over the whole temperature range, whilst that of pyrites ceases to agree at higher temperatures.

J. F. S.

Theory of Space Grating Oscillations and the Specific Heat of Solid Substances. HANS THIERING (*Physikal. Zeitsch.*, 1913, 14, 867—873. Compare Born and Kármán, *Physikal. Zeitsch.*, 1912, 13, 297, and this vol., ii, 101).—The author shows that the equation deduced by Born and Kármán on the specific heat of regular crystalline substances can be strictly developed mathematically. The specific heat of copper, rock salt, and sylvine is calculated for low temperatures, and values obtained which in cases differ from the observed values of 6—16%. These divergencies can in every case be explained theoretically.

J. F. S.

Atomic Specific Heats between the Boiling Points of Liquid Nitrogen and Liquid Hydrogen. I. Mean Atomic Specific Heats at 50° Absolute of the Elements a Periodic Function of the Atomic Weights. SIR JAMES DEWAR (*Proc. Roy. Soc.*, 1913, 4, 89, 158—169).—The specific heat of 53 elements

has been determined between the temperatures of boiling nitrogen and boiling hydrogen. The substances were cut into pieces of uniform shape, and cooled in a jacket containing liquid nitrogen; they were then allowed to drop into a calorimeter containing liquid hydrogen, and the volume of hydrogen gas given off was measured. After a number of corrections were applied the specific heat was calculated, and it is shown that the specific heat is a periodic function of the atomic weight, and that the atomic specific heat curve has a similar form to the Lothar Meyer atomic volume curve.

J. F. S.

Specific Heat of Hydrated Salts. LUIGI ROLLA and LUIGI ACCAME (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 109—116).—An expression for the difference of the specific heats of the last molecules of water of crystallisation of two hydrated salts may be deduced from thermodynamical considerations. By experiment the molecular heat of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ at 9° is found to be 93.66, that of $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ 80.75, so that the last molecule of water has a molecular heat of 12.91 cal. (calculated 12.91). The molecular heat of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ is found to be 79.657 cal., and, Kopp's value for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ being 88.97, the molecular heat of the last molecule of water is 9.31 (calculated 10.09). The author's experiments, however, give a value for the molecular heat of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ which would reduce the value for the difference from that of the hexahydrate to 6.86 cal. Measurements of the molecular heat of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ give 92.147 and 63.587 cal. respectively, the difference being 28.56 (calculated 27.16). R. V. S.

Determination of the Freezing Point. A. VAN RAALTE (*Chem. Weekblad*, 1913, 10, 709).—A description of a perforated, metallic cylinder recommended as a protection for the glass tube employed in cryoscopic work.

A. J. W.

Apparatus for the Determination of Boiling Points. A. A. BESSON (*Chem. Zeit.*, 1913, 37, 1035).—The apparatus is so arranged that the thermometer does not come into contact with the condensed liquid falling back into the flask from a return condenser. This is attained by placing the thermometer in a wide tube opening through the stopper of the flask. At the upper end of this tube is a side-tube, through which the vapours pass, connecting with another wider tube; the end of the condenser opens into the top of this wider tube, the bottom of which connects with a narrow tube leading through the stopper to the bottom of the flask, thus allowing the condensed liquid to return to the flask without coming in contact with the thermometer.

T. S. P.

Determination of the Vapour Pressure and Density Curves of Oxygen; Construction of an Apparatus for Determining Critical Data. F. E. E. GERMANN (*Physikal. Zeitsch.*, 1913, 14, 857—860).—An apparatus designed by Nerst and Eucken is employed. The temperature measurements are made by means of

a lead resistance thermometer, which is shown to change its resistance more regularly than platinum in the region 20—60° absolute, and can be read to 1/100 of a degree. It is shown that a vacuum vessel can be kept at a constant temperature by the use of liquid air and an electrical heater simultaneously. Using this apparatus the vapour-pressure curve of oxygen has been determined for pressures from 1 to 25 atmospheres. The density of liquid oxygen over the same pressures has also been obtained, and the values found to lie between 1.0605 at 2.72 atms. and 100.25° absolute and 0.8474 at 23.59 atms. and 136.10°. J. F. S.

Vapour-pressure Curve of Oxygen and the Determination of the Critical Data of Hydrogen. FRITZ BULLE (*Physikal. Zeitsch.*, 1913, 14, 860—862).—Using a slightly modified Nernst-Eucken apparatus, the author has determined the vapour-pressure curve of oxygen, and obtained values which do not differ more than 1/10° from those of Germain (see preceding abstract). By means of the same apparatus the critical constants of hydrogen have been determined, and the values critical temperature $31.95^{\circ} \pm 0.10$ and critical pressure 11.0 atm. have been obtained. J. F. S.

Fixed Points in Thermometry between 100° and 400°. Vapour Tensions of Naphthalene, Water, and Benzophenone. I. Vapour Tensions of Naphthalene. J. M. CRAFTS (*J. Chim. phys.*, 1913, 11, 429—477).—The boiling point of water is suitable as a thermometric standard for temperatures between +70° and +170°. Only two substances, namely, naphthalene and benzophenone, have been found sufficiently stable for use above +170°. Naphthalene, purified by fractional crystallisation, retained its boiling point unaltered after boiling continuously for twelve months. The boiling point was 218.25°, 219.09°, and 218.46° on different mercurial thermometers.

A complete series of pressure-boiling point values for naphthalene was obtained by direct comparison with a constant volume nitrogen thermometer between 231.16 mm. (+171.23°) and 2149.31 mm. (+269.51°), and an interpolation formula worked out which satisfactorily covers the whole of this range.

The specially designed ebullioscope charged with one kilo. of naphthalene was mounted as nearly horizontally as possible to avoid the error due to the weight of the vapour column. The naphthalene vapour was liquefied in a condenser maintained at +80° by circulating water. The variation in temperature from one part of the vapour space to another was less than 0.01°.

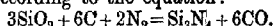
The thermometer filled with atmospheric nitrogen was used in conjunction with a special form of open-type manometer, and a syphon barometer in which the levels were determined electrically with great precision by platinum contact points attached to the verniers. For pressures less than atmospheric the syphon barometer was used alone as a manometer. The average temperature of the mercury column was indicated by a thermometer the bulb of which was of the same dimensions as the whole barometer

After every measurement the fixed points 0° and 100° of the gas thermometer were redetermined so as to avoid errors due to the hysteresis of the glass.

The boiling point of naphthalene at 760.00 mm. is 218.06° at 28 metres above sea level at the latitude of Boston, U.S. ($42^{\circ}21'$).

R. J. C.

Heat of Formation of Silicon Nitride. CAMILLE MATIGNON (*Bull. Soc. chim.*, 1913, [iv], 13, 791—793).—Silicon nitride is formed by heating a mixture of silica and carbon in a stream of nitrogen at 1400 — 1500° according to the equation:



When using a mixture of nitrogen with 30% of carbon monoxide the author finds that union with nitrogen proceeds at 1500° , but not at 1400° , and that it appears to commence at 1450° . He thus deduces that the system is in equilibrium between 1400° and 1450° for this pressure of carbon monoxide. By substituting the values so obtained in Nernst's formula, he calculates the heat of formation of silicon nitride to be 159.3 Cal.

H. W.

Stability of Cyclic Compounds from a Thermochemical Point of View. P. V. ZUBOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 753—766. Compare A., 1902, i, 144).—By dividing the molecular heats of combustion of ethylene, cyclopropane, etc., by 2, 3, etc., the author obtains the heat effect corresponding with CH_2 . Some of the values thus derived are as follows:

Ethylene	166.65 Cals.	Propylene.....	164.23 Cals.
cycloPropane	166.47 "	Methylcyclobutane	159.98 "
cycloPentane.....	159.86 "	Methylcyclopentane.....	159.49 "
cycloHexane.....	159.20 "	Methylcyclohexane.....	159.28 "
cycloHeptane	158.80 "	Methylcycloheptane	159.19 "

Other series of homologous derivatives give similar results.

It is seen that the interatomic linkings in the different rings are not identical, and that the heats of formation increase from the lower to the higher rings.

Comparison of these heat effects for the cyclic carboxylic acids with those for the corresponding hydrocarbons shows that replacement of one or more carboxyl groups by one or more hydrogen atoms is accompanied by no appreciable change in the heat of combustion.

Stohmann and Kleber (A., 1892, 1040) are of the opinion that the stability of atomic rings may be measured by the heat effects observed when cyclic compounds are converted into open-chain compounds by combination with a molecule of hydrogen. Such a conclusion is, however, controverted by Stohmann's own results, which showed that the amount of heat developed on rupture of a four-carbon atom ring varies with the position of rupture. A similar refutation is furnished by the author's results., T. H. P.

Sublimation of Metals at Low Pressures. GEORGE W. C. KAYE and DONALD EWEN (*Proc. Roy. Soc.*, 1913, A, 89, 58—67. Compare Harker and Kaye, this vol., ii, 661).—The disintegration

of a number of metals by heat is examined. It is shown that when heated to 950°, copper, iron, and tungsten are disintegrated, and emit particles at right angles to their surface, leaving an etched surface. This emission of particles is distinct from the natural volatilisation, and is more marked when the heating is effected by passing a direct current through the metal than when the heating is external to the metal. A number of theories are considered to account for the disintegration, and it is suggested that particles are charged and a repulsion causes the disintegration. The results are regarded as of a preliminary nature. J. F. S.

Some of the Conditions Affecting Explosions of Coal Gas and Air. I. E. L. SELLARS and C. CAMPBELL. II. E. L. SELLARS (*J. Soc. Chem. Ind.*, 1913, 32, 730—736).—The gas mixture used in the experiments contained 12.3% of coal gas. The propagation of the explosions was effected in glass tubes varying from 4 to 18 metres in length; for measuring the rate of propagation each tube was marked at every metre, and the time noted, by means of a special registering apparatus, at which the flame passed each mark.

Part I. deals with the initial velocity of explosion, by the initial velocity being meant the velocity with which the flame travels through that portion of the initial uniform period, where oscillations have not begun. Increase in diameter of tube means an increase in the initial velocity of a flame started by sparking near an open end of a tube, whether the further end be open or closed. The effect of increasing the length of the tube, keeping the diameter constant, on the initial velocity of a flame produced by sparking near an open end is, in the case of the further end being closed, to cause a slight decrease; when the further end is open the length has no effect. If the flame is started by sparking near an open end, the fact of the further end being closed causes the initial velocity to be slightly greater than it would be if the further end were open. The initial velocity is fairly constant.

Part II. deals with the rate of explosion, as affected by the length and diameter of the tube, by the position of the spark, and by the material of the tube, etc. The conclusions arrived at are summarised as follows: The conditions of the tube in which the explosion takes place greatly affect the distance the flame travels. The state in which the ends of the tube are put, that is, whether open or closed, may change the whole character of an explosion; for example, a flame started near an open end of a tube may be quite feeble, and the velocity slow, whereas if the flame were started near the same end, closed before ignition, the explosion might travel with considerable violence and velocity. This shows the possible effect of a closed passage on an explosion in a mine. Increase in length of the tube increases the rate of explosion up to a certain limit; in tubes less than a certain minimum diameter (10 mm., with the gas mixture used) the flame will not propagate itself. Sparking near an open end, the further end being closed, the flame travels

with a somewhat greater velocity in a lead tube than in a glass tube, although the general character of the flame is unaltered.

T. S. P.

The Freezing of Nitroglycerol [Glyceryl Trinitrate]. The Heat of Transformation of the Nitroglycerol Isomerides. HAROLD HIBBERT and G. PRESCOTT FULLER (*J. Amer. Chem. Soc.*, 1913, 35, 978—989).—The recently published experimental results on the existence of two crystalline forms of glyceryl trinitrate (Hibbert, this vol., i, 817) indicated that of the changes liquid phase \rightarrow labile solid phase and labile solid phase \rightarrow stable solid phase the latter was accompanied by far the greater thermal change. As the only work in this direction is that of Nauckhoff (*Zeitsch. angew. Chem.*, 1905, 18, 17), who estimated the heat development for the transformation liquid phase \rightarrow stable solid phase, the authors have applied the Bunsen ice-calorimeter to the measurement of the heat development in the above two changes.

The heat of transformation of 1 gram of liquid glyceryl trinitrate into the labile solid isomeride was found to be 5.2 calories, whilst that of the labile into the stable solid isomeride was 28.0 calories; from these figures 33.2 calories must be developed during the crystallisation of liquid glyceryl trinitrate into the stable solid form, this result diverging considerably from that of Nauckhoff, who found 23.1 calories for the change at 1.5°.

Although the labile isomeride at 0° is rapidly converted into the stable one if a little of the latter is well incorporated in it, mere contact with a crystal of the stable form requires twenty-five to thirty-five minutes to effect a complete transformation. D. F. T.

A Combination Specific Gravity Bottle and Dilatometer. CHARLES ALBERT BROWNE (*J. Amer. Chem. Soc.*, 1913, 35, 955—958).—The specific gravity bottle is a U-shaped pyknometer, the one limb of which is made of wide tubing, into which is ground a thermometer, which at the same time acts as a stopper; the graduated part of the thermometer is completely inside the tube. The other limb is made of capillary tubing, and is graduated; it is fitted with a ground-on stopper. When the wide limb is completely filled with liquid, any change in volume caused by a reaction occurring in the liquid can be measured by readings made on the narrow limb. In this way, for example, the contraction which sugar solutions undergo during hydrolysis or inversion can be measured. T. S. P.

Density at Absolute Zero and Critical Density of Several Gases. MAURICE PRUD'HOMME (*J. Chim. phys.*, 1913, 11, 520—528). Compare this vol., ii, 298).—The sum of the three densities corresponding with the three volumes in van der Waal's equation is constant and equal to the density at absolute zero, which must be either three or four times the critical density; thus $d_1 + d_2 + d_3 = D_0 = 3D_c$ or $4D_c$. In the former case, at the critical point $d_3 = D_c$ and in the latter $d_3 = 2D_c$. Now d_3 has been interpreted as mean

ing the density of the surface film between liquid and gas, and it is probable that although $d_s = 2D_c$ in the series of esters, etc., studied by Young, it would be found with simpler substances which approximate to perfect gases that $d_s = D_c$.

Sulphur dioxide falls into this class, since on passing from 420° abs. to 280° abs. the value of n in the equation:

$$d_1 + d_2 = 4D_c - 2D_c(T/T_c)^n$$

approaches unity. With sulphur dioxide, therefore, the density at absolute zero $D_0 = 4D_c$.

In the cases of nitrous oxide and carbon dioxide the densities are in better accord with an expression of the form

$$d_1 + d_2 = 3D_c - D_c(T/T_c)^n,$$

whence $D_0 = 3D_c$ for these gases.

R. J. C.

The Weight of a Falling Drop and the Laws of Tate. XI. The Drop Weight and Surface Tension of Blood Serum. J. LIVINGSTON R. MORGAN and HAROLD E. WOODWARD (*J. Amer. Chem. Soc.*, 1913, 35, 1249—1262).—The authors have applied the drop-weight method to the determination of the surface tension of blood serum, and obtained the following results: The surface tension of blood serum in an individual may change during the day, depending on the food which is being absorbed by the blood. It is approximately the same (about 45.4 dynes per cm. at 37°) in different individuals and different species, if account be taken of the possibility of a daily change in any one individual. In certain diseases, especially those in which the kidneys are affected, the surface tension is abnormally high.

Ascoli and Tzar's meiostagmin reaction was found to be positive in more than 80% of the cases of clinically positive syphilis investigated; in those cases where it was not positive, the Wassermann test was either weak or doubtful.

T. S. P.

The Meyer Molecular Weight Calculation. PERCY N. EVANS (*J. Amer. Chem. Soc.*, 1913, 35, 958—959).—In carrying out a determination of vapour density by V. Meyer's method, it is usual to correct for the vapour tension of water when correcting the volume of expelled air to N.T.P. This is only correct when the original air in the apparatus is quite dry. If it is moist, the corrected barometric pressure is $B - (100 - H)w/100$, where B is the barometric reading, H is the percentage of saturation at room temperature, as determined with a hygrometer, and w is the pressure of aqueous vapour. If the air used is saturated, there is no correction to be applied to the barometric pressure. In damp, warm weather, the application of the correction usually made may lead to an error of 1 in 45.

T. S. P.

A Viscometer for Volatile Liquids. J. P. KUENEN and S. W. VISSER (*Proc. K. Akad. Wetensch., Amsterdam*, 1913, 16, 75—84).—The authors have constructed a viscometer, based on the Ostwald instrument, for use with volatile liquids. The vertical capillary

has the usual bulb with two marks at the top, and projects into a larger bulb at the bottom. The wide tube is sealed on near the top of the lower bulb, and bent round and sealed to the top of the higher bulb, thus forming a closed apparatus. A side-tube, for admitting the experimental liquid, is attached to the wider tube. The apparatus has been tested for water at various temperatures, and the influence of varying the volume of the liquid has been worked out. The correction for capillarity, due to the capillary dipping into the lower liquid, is also determined. A German silver bath for use with the apparatus at low temperatures is described. Preliminary measurements were made with *n*-butane, and the following figures for η obtained: 34.5°, 0.00163; 18.5°, 0.00176; 0.0°, 0.00207; -23.6°, 0.00265. From these values it is shown that the viscosity at the boiling point corresponds well with the values found by Thorpe and Rodger for other hydrocarbons (T., 1894, 65, 782). J. F. S.

Internal Friction of Binary Systems. B. P. WEINBERG (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 701-706).—The author has calculated for the three binary systems (1) allylthiocarbimide and piperidine, (2) phenylthiocarbimide and diethylamine, and (3) allylthiocarbimide and methylaniline, and for various ranges of temperature the values of $\alpha = (\eta_1 - \eta_2) / \eta_2(t_2 - t_1)$ (compare Kurnakov and Shemtschushni, this vol., ii, 190), and those of a in the formula $\eta_2 = \eta_1 : \alpha^{t_1 - t_2}$, which has been employed by various authors to express the dependency on the temperature of the coefficient of internal friction of solids and supercooled liquids.

For the mixtures containing the two components in equimolecular proportions the magnitude of α varies widely for different intervals of temperature, and on this account preference is to be accorded to the second of the above expressions, the values of a showing considerably greater constancy. Further, the variations of the values of a from 1 are similar to those obtained with liquids supercooled by some tens of degrees, and the superiority of these values over those for the separate constituents explains the appearance of the maxima in the curves of the temperature-coefficients constructed by Kurnakov and Shemtschushni.

These considerations lead the author to the opinion that when equimolecular proportions of the constituents of systems (1), (2), and perhaps also (3) are brought into contact, the corresponding compounds are obtained directly in the form of supercooled liquids. Mixtures in proportions other than equimolecular may be regarded as solutions of these supercooled liquids in one of the two solvents which, being of considerably lower viscosity, causes a marked decrease in the coefficient of internal friction.

The change produced in the value of η for such an equimolecular compound by dilution with one of the two solvents may be represented by $p = (\log \eta_m - \log \eta_1) / (\log \eta_0 - \log \eta_1)$, where η_m is the coefficient of viscosity with a content of m gram-mols. of solvent per $(1 - m)$ gram-mols. of dissolved substance. Calculation of p

for the systems mentioned above shows that, as a first approximation, $p=m$.

These considerations necessitate certain modifications in the explanations advanced by Kurnakov and Shemtschushni for some of their results.

T. H. P.

The Chemical Interpretation of Special Points on Curves. L. GAY and F. DUCELLIEZ (*Bull. Soc. chim.*, 1913, [iv], 13, 783—784). Compare this vol., ii, 387).—A reply to Kolosovski (compare this vol., ii, 674).

H. W.

Viscosity of Chlorinated Aliphatic Hydrocarbons and Their Mixtures. WALTER HERZ and W. RATHMANN (*Zeitsch. Elektrochem.*, 1913, 19, 589—590).—The viscosities of a number of chlorinated hydrocarbons have been measured at different temperatures. The following values are recorded: *cis*-Dichloroethylene η at $25^\circ=0.437$; *trans*-dichloroethylene η at $25^\circ=0.615$, at $50^\circ=0.812$, at $75^\circ=0.976$; tetrachloroethylene η at $25^\circ=0.940$, at $50^\circ=1.194$, at $75^\circ=1.404$; tetrachloroethane η at $25^\circ=1.808$, at $50^\circ=2.033$, at $75^\circ=2.154$; and pentachloroethane η at $25^\circ=2.432$, at $50^\circ=2.635$, at $75^\circ=2.789$. Several mixtures were examined at 25° ; the mixture trichloroethylene and pentachloroethane gives a viscosity-composition curve which is a straight line lying between the values of the constituents; tetrachloroethylene and carbon tetrachloride gives a curve in which a maximum occurs, and tetrachloroethane and carbon tetrachloride gives a curve slightly convex to the composition axis. The densities of the various mixtures have also been determined.

J. F. S.

Viscosity of Emulsoid Sols and its Dependence on the Velocity of Shearing. EMIL HATSCHEK (*Kolloid. Zeitsch.*, 1913, 13, 38—96. Compare this vol., ii, 559).—The viscosity of gelatin and starch sols has been determined at different shearing velocities by means of a modified Couette apparatus previously described (*loc. cit.*). With $\frac{1}{2}\%$ of gelatin sol it is shown that in a given case the viscosity value 2657 with a shear velocity of 3.52° fell to the value 1316 on increasing the shear velocity to the maximum value for tranquil shearing, but on reversing the process, by decreasing the velocity, the viscosity rose again to 3822, thus indicating a marked hysteresis. In the case of a potato starch sol the viscosity of 730 was obtained at the maximum velocity of 40.1° , and this with decreasing velocity increased until at 24.5° it reached the value 1233; at this point with further decreasing velocity a rapid decrease in viscosity occurred until at the minimum velocity the value 779 was reached. The velocity was then slowly increased, and the viscosity fell further, until at 52.9° it had reached 364, and at this point with increasing velocity it rose to 80. The results show that the viscosity is not a constant quantity, and calculations applied to the capillary viscometer show that such measurements made by a capillary viscometer under the same external conditions cannot be regarded as being carried out under

comparable conditions, for if a definite shear velocity is exceeded, disturbances in the sol under examination will take place.

J. F. S.

Theory of Dyeing. The Partition of Colour Substances Between Two Solvents. WILLEM REINDERS (*Kolloid. Zeitsch.*, 1913, 13, 98—105).—The author discusses the three theories of dyeing, and a series of partition experiments with a series of organic colouring matters are carried out between water and isobutyl alcohol. In many cases the aqueous layer is either acidified or made alkaline. The experiments were carried out with methylene-blue G. (conc.), methylene-blue D., magenta, crystal-violet, new magenta, crystal-ponceau, patent blue, erythrosin, roccellin, quinoline yellow, alkali blue, and Congo red. It is shown that the simple partition relationship does not exist in any case, but that in some cases the factor $1/n$ of the adsorption relationship $x/m = ac^{1/n}$ is constant, and generally less than unity. The relationships observed in the case of a colouring matter and fibre are compared with the experimental results, and the conclusion is drawn that the taking up of a dye by a fabric consists mainly in the formation of a solid solution, and the assumption of the formation of an adsorbed layer is unnecessary.

J. F. S.

The Form of the Ideal Electro-capillarity Curve. F. KRÜGER and H. KRUMREICH (*Zeitsch. Elektrochem.*, 1913, 19, 617—622).—The form of the electrocapillarity curve is determined for potassium nitrate and potassium nitrate containing mercurous nitrate, and is shown to be an exact parabola. This result is in agreement with the electrical theory of electrocapillarity of Lippmann, Helmholtz, and Nernst. The capacity of the double layer is calculated from this parabola, and found to be 27 microfarads.

J. F. S.

The Theory of Cohesion Pressure and the Lipoid Theory. ISIDOR TRAUBE (*Biochem. Zeitsch.*, 1913, 54, 305—315).—The author recapitulates his theory of osmosis of substances into cells, which forms the basis of his previous investigations, and calls attention to the fact that so many of the more recent biological investigations on narcosis, plasmolysis, effect of substances on the oxydones, etc., are in better accord with this theory than with the lipoid theory of Overton and Meyer. He calls attention also to the fact that on account of their capacity to lower the surface tension of an aqueous solution, many substances may be readily taken up by lipoids from water. The solubility in lipoids is not, however, the main factor in the various phenomena.

S. B. S.

Relation Between Viscosity and Heat of Fusion. J. DE GUZMÁN (*Anal. Fis. Quim.*, 1913, 11, 353—362).—The relation is expressible by the equation $d \ln \phi / dT = W/RT^2$, where ϕ is the coefficient of viscosity, and W the molecular heat of fusion.

G. D. L.

Law of Capillary Ascent. VLADIMIR A. KISTIakovSKI (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 782—801).—The author advances a theoretical explanation of his capillarity rule (*A.*, 1906, ii, 655). Experimental data are given for 141 compounds, including almost all the non-associated liquids yet investigated, satisfactory agreement with the rule being shown in all cases.

It is shown theoretically that, with non-associated liquids, the molecular weights calculated by means of this rule hold for the compound in both the liquid and gaseous phases.

With associated liquids it is impossible to make direct application of the value of the constant for the calculation of their degrees of association.

The results obtained show that the capillarity method is to be recommended for determining the molecular weights in the liquid or gaseous phase of aliphatic and aromatic hydrocarbons and their halogenated derivatives, aliphatic and aromatic amines, ethers and esters, aromatic aldehydes and ketones.

T. H. P.

Theory of Narcosis. ISIDOR TRAUBE (*Pflüger's Archiv*, 1913, 153, 276—308. Compare *A.*, 1905, ii, 13; 1908, ii, 565; 1912, ii, 740; Overton, *A.*, 1897, ii, 337).—A theoretical paper in which previously published work of the author and others is considered in connexion with the theory of narcosis. It is shown that narcotics are substances of small cohesion pressure in water, which consequently lower the surface tension and internal pressure of water and aqueous cell fluids, and raise the vapour pressure of the same liquids. If the cohesion pressure of a volatile narcotic in water is very small or almost zero, the lowering of the surface tension of the aqueous solution does not furnish an accurate measure of the cohesion pressure. In such cases a great decrease of the internal pressure takes place on account of the fine emulsion produced by such narcotics. Narcotics of this type possess a marked vapour pressure, both alone and in contact with water. The more a narcotic reduces the surface tension, the smaller is its cohesion pressure, and the more easily it is dissolved in lipidic substances, absorbed by other surfaces, and "di-smosed" into the inside of cells even when the walls of such cells do not contain lipoids. There is no regularity between the lowering of the surface tension on the one hand, and lipid solubility and absorption by non-lipoid substances on the other. The increase in lipid content of the cells has an influence on the velocity of absorption of narcotics, and consequently on the intensity of their narcotic action, but the lipid content is not the cause of the increased absorption and action, for lipid-free cells can be brought under the influence of narcotics. The more a narcotic of small cohesion pressure in water lowers the surface tension and internal pressure of cell fluids, the more it changes the physical condition of the dissolved substances, for example, colloidal particles aggregate, and their solubility is decreased. Such change of condition of proteins, nucleoproteins and lipoids, and also the smaller pressure inside the liquid, have

the effect of retarding or stopping certain chemical reactions, such as oxidation. The space in which these reactions occur, and the dead space of Liebreich will be increased by the presence of narcotics. These conditions become of more importance in the polyphase lipid regions (nerve cells), since the size and surface of the phases is increased by the semi-coagulation. Since the narcotics concentrate on the surface of separation of the cell wall from the cell liquid, they reduce the electric contact potential, and consequently directly retard the transmission of movement and sense impulses to the nerve centres. The retardation which substances of small cohesion pressure in water exercise on oxidation and other chemical reactions, and also on the electrical surface processes, is the cause of the conditions which are generally known as narcosis.

J. F. S.

Narcosis. ISIDOR TRAUBE (*Biochem. Zeitsch.*, 1913, 54, 316—322).—The author criticises chiefly recent papers by Vernon (this vol., i, 802) and Winterstein (*ibid.*, i, 785). According to Czapek's statement, the main factor influencing exosmosis from certain plant-cells is the surface tension (measured against air) of the surrounding solutions. In the case of *Echeveria*, tannin exosmosis takes place when this surface tension is about 0.67 (water=1). Vernon has objected to this conception of osmosis, which is in accordance with Traube's theory, in that there are several exceptions. The author attempts to explain these exceptions in some detail. He is in agreement with Winterstein in the view that narcosis cannot be explained simply as a phenomenon of asphyxia.

S. B. S.

A New Principle for the Direct Determination of Osmotic Pressure. ERNST COHEN and G. DE BRUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 160—161).—A porous pot holding a semi-permeable medium is filled with the solution to be examined, and closed by a stopper through which passes a capillary tube and a copper wire supporting a copper electrode. A second copper electrode is placed in the surrounding water vessel. The porous pot is then immersed in the water, and the liquid immediately begins to rise in the capillary. An *E.M.F.* just sufficient to prevent the liquid rising any further is then applied to the electrodes, and the height of the liquid in the capillary measured. If h_1 represents the height of the liquid in the capillary and E_1 the counterbalancing *E.M.F.*, and P the osmotic pressure, then $P - h_1 = kE_1$, where k is a constant. On breaking the current circuit the liquid rises again to, say, h_2 ; an *E.M.F.* is then again applied to counterbalance this, say, E_2 . From this, $P - h_2 = kE_2$; hence

$$P = h_1 + (h_1 - h_2)E_1/(E_2 - E_1).$$

The advantages of this method are: (1) The short time required for the determination; (2) the durability of the membrane, since it has a pressure on both sides; and (3) the absence of volume change of the solution by the entrance of the solvent. J. F. S.

Use of Toepler's Differential Manometer in Studying the Diffusion of a Gas. R. FOCH (*Ann. Chim. Phys.*, 1913, [viii], 29, 597—613).—The author has attempted to measure the rate of diffusion of carbon dioxide into air, using a differential manometer consisting of a U-tube of very obtuse angle, charged with xylene. One end of the manometer is connected with the air, the other with the tube from which diffusion is taking place. The movements of the xylene meniscus are recorded photographically, a full description of the necessary apparatus being given. Errors are found to arise from unsuitable atmospheric conditions, variations in temperature of the meniscus due to the illumination necessary for photographic purposes, solubility of carbon dioxide in xylene, irregularities in the manometric tube, and the inertia and viscosity of the liquid. Of these, the first is the most important, and can only be overcome by waiting for calm days. The second is largely avoided by reducing the period of illumination by placing the pendulum between the source of light and the manometer. The third source of error is eliminated by thoroughly cleansing the apparatus before each experiment; under these conditions the carbon dioxide does not come into contact with the xylene. The fourth is avoided since the errors involved occur in either direction, and can be eliminated by taking a sufficiently large number of readings, whilst the effect of the fifth can be evaluated for any particular state of the manometer, especially if the liquid is not renewed.

Experiments with carbon dioxide have shown that its coefficient of diffusion is constant from the start of the experiment. Its exact value can only be determined with an apparatus which can be more precisely calibrated.

H. W.

Thermal Effects Produced by Heating and Cooling Palladium in Hydrogen. J. H. ANDREW and A. HOLT (*Proc. Roy. Soc.*, 1913, A, 89, 170—186).—The authors have plotted the cooling and heating curves of palladium of various kinds in a vacuum and in hydrogen. It is shown that palladium is dimorphic, the stability of the two forms depending on the temperature. The rate of change of the one form into the other is extremely slow. The initial rapid occlusion of hydrogen is probably due to the presence of the amorphous form of palladium, and in the absence of such an amorphous film, palladium may be quite passive with regard to rapid occlusion of the gas in the cold. It is probable, however, that the passivity is apparent rather than real, and that if sufficient time were allowed for occlusion to take place a volume of gas equal to that occluded by active palladium would pass into solution. At temperatures above 100° a rapid occlusion of a small quantity of hydrogen occurs with both forms of palladium with the development of a constant quantity of heat. Both varieties of palladium cease to absorb hydrogen above a certain temperature, and above 150° they both have an equal affinity for the gas. J. F. S.

Physico-chemical Study of Neutralisation. EUGÈNE CORNEC (*Ann. Chim. Phys.*, 1913, [viii], 29, 490—540, 30, 63—163. Compare A., 1909, ii, 972).—The author has studied the variation of the freezing point of solutions of various acids during neutralisation by a solution of a base of the same molecular concentration. The results are graphically represented by taking depressions of the freezing point as ordinates and composition of the mixtures as abscissae.

In the case of the neutralisation of monobasic acids (hydrochloric, chloric, perchloric, acetic, phenol) by a strong base (potassium or sodium hydroxides) the diagrams obtained are composed of two almost straight lines, the intersection of which corresponds with the normal salt. The cryoscopic method thus indicates the completion of neutralisation.

In the case of polybasic acids (sulphuric, oxalic, carbonic, resorcinol, arsenic citric), neutralised by potassium or sodium hydroxide, complete neutralisation is indicated by a minimum depression of the freezing point, and the position of this minimum indicates the basicity of the acid. Phosphoric, phosphorous, and hypophosphorous acids thus appear to be tribasic, dibasic, and monobasic respectively.

The cryoscopic method allows the detection, not merely of acidity which is too weak to be detected by methyl-orange, but even of such acidity as is not indicated by phenolphthalein (for example, the second acidity of carbonic acid). It is, however, not infallible. Certain very weak acidities, such as the second of hydrogen sulphide or the third phenolic group in pyrogallol, escape detection.

When potassium or sodium hydroxide is replaced by ammonia, analogous results are generally obtained. Certain acidities, indicated by the use of a strong base (the third of phosphoric or arsenic acids), are not shown when ammonia is employed.

In addition to the normal salts which are indicated with great clearness, the cryoscopic diagrams frequently show the formation of acid salts by breaks in the curve, which, however, are not generally well marked. In certain cases the existence of these breaks is doubtful, whilst in other instances they do not appear at all. The so-called abnormal acids salts, such as $\text{KH}_2(\text{PO}_4)_2$, $\text{K}_7\text{H}_6(\text{PO}_4)_4$, $\text{K}_5\text{H}_4(\text{PO}_4)_3$, are never indicated.

An exhaustive comparison is made between the results obtained by the above method and those derived from determinations of the electrical conductivity of similar solutions. The two methods do not yield the same results, but are complementary the one to the other. In the determination of basicity, the cryoscopic method is to be preferred.

In a number of cases the variation of the index of refraction during the course of neutralisation has been studied. When citric acid is neutralised by sodium hydroxide, the existence of the normal citrate is shown, and similar results are obtained when ammonia is used. With phosphoric acid and potassium hydroxide, evidence of the formation of monopotassium and tripotassium phosphate is

obtained (compare Féry, A., 1893, ii, 201). When ammonia is used, on the other hand, the mono- and di-ammonium salts are indicated, no certain evidence of the tri-ammonium salt being obtained. When phosphorous acid is neutralised by potassium hydroxide, the formation of the mono- but not of the di-potassium salt is shown, whilst, with ammonia, the diammonium salt is sharply indicated. With carbonic acid, evidence of the formation of the normal salt is obtained, but less definitely than when the cryoscopic method is utilised.

In the case of phosphoric acid, the variation of density during neutralisation has been similarly employed. When potassium hydroxide is used as base, evidence of the existence of mono- and tri-potassium phosphates is obtained. Indications of the formation of abnormal acid salts in solution are not obtained by this method.

Iodic acid, when neutralised with potassium hydroxide, gives a minimum depression at a point corresponding with the formation of the normal salt. A similar result is obtained by observations of the refractive index of a solution of the acid when treated with sodium hydroxide. Evidence of the existence of an acid salt is not obtained in either case. Experiments on the freezing points of aqueous solutions of iodic acid and of sodium iodate, in conjunction with the results obtained by comparative determinations of the electrical conductivity of chloric, bromic, and iodic acids, lead the author to the conclusion that the latter is probably polymerised in concentrated aqueous solution.

From observations of the depression of the freezing point during neutralisation with potassium hydroxide and of the index of refraction when neutralised with sodium hydroxide, dithionic acid appears to be dibasic. This is confirmed from determinations of the freezing point of solutions of potassium dithionate and of the freezing point and electrical conductivity of solutions of the free acid.

A cryoscopic study of the neutralisation of pyrophosphoric acid by potassium hydroxide or ammonia only indicates the existence of the normal salt, $M_2P_2O_7$. The curves for the index of refraction show definite breaks corresponding with the di- and tetra-salts, whilst, if potassium hydroxide is used as base, indications of the existence of the salt, $K_4HP_2O_7$, are also obtained.

Hypophosphoric acid corresponds with the formula $H_2P_2O_6$, a result which is confirmed by cryoscopic determinations of the solution of the acid (compare Rosenheim, Stadler, and Jacobsohn, A., 1906, ii, 744; Parravano and Marini, *ibid.*, 744; Rosenheim and Pritze, A., 1908, ii, 942; Cornec, A., 1910, ii, 122).

Solutions obtained from ordinary or crystalline phosphoric oxide, from vitreous metaphosphoric acid, or from lead metaphosphate invariably contain a certain amount of pyrophosphoric in addition to metaphosphoric acid. The latter substance in these solutions is polymerised, having at least the complexity indicated by the formula $(HPO_3)_3$, but the exact degree of polymerisation could not be ascertained (compare Holt and Myers, T., 1911, 99, 384).

Selenious acid behaves as a mixed dibasic acid; the solutions

obtained by half-neutralisation contain the acid selenites, MHSeO_3 , and not the pyroselenites, $\text{M}_2\text{S}_2\text{O}_5$.

Boric and arsenious acids are monobasic in solution, but no decision can be arrived at between the formulæ HBO_2 or H_3BO_3 and HAsO_2 or H_3AsO_3 . The cryoscopic curve of boric acid gives evidence of the formation of condensed salts in solution.

Sucrose appears to combine with sodium hydroxide in aqueous solution to form a salt which can only exist in equilibrium with the products of its decomposition by water.

In the cases of chromic and periodic acids, cryoscopic curves of a peculiar kind are obtained, showing that, for these acids, the phenomenon of neutralisation is complicated by a reaction between the normal salt and an excess of base leading to the formation in solution of salts corresponding with different acids. An aqueous solution of chromium trioxide contains the acid $\text{H}_2\text{Cr}_2\text{O}_7$, the normal salt of which, $\text{Na}_2\text{Cr}_2\text{O}_7$, reacts with sodium hydroxide to yield Na_2CrO_4 , the normal salt of the unknown acid, H_2CrO_4 .

Periodic acid has the formula HIO_4 , and yields with one molecular proportion of potassium hydroxide the normal salt, KIO_4 ; a second molecular proportion of base converts this into the salt, $\text{K}_4\text{I}_2\text{O}_9$; a third proportion again reacts, yielding a salt which does not contain more than one atom of iodine in its molecule. H. W.

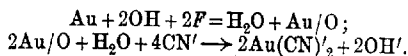
Limits of Visibility of Precipitates. LUIGI ROLLA (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 104—108).—In the case of silver haloids, the author has verified the fact that the limits of their visibility in solution measured with the ultramicroscope coincide with their solubilities as determined electrochemically. By the same optical method he has measured the limits of visibility of some mercurous salts, in regard to some of which the electrochemical results have been discordant. He obtains for the limit of visibility (or solubility) at $17-18^\circ$ the following values: HgCl 4.5×10^{-6} , HgNO_3 5×10^{-6} , HgBr 3×10^{-7} . The value found for mercurous chloride accords with certain theoretical considerations with which none of the values of this constant previously obtained has been in agreement. R. V. S.

Retardation in the Solution of Gold and Silver in Aqueous Cyanide Solution. IVAN IV. ANDRÉEV (*Zeitsch. Elektrochem.*, 1913, 19, 667—672).—The influence of the addition of oxidising agents on the rate of the solution of gold and silver in dilute cyanide solution has been determined. The experiments were carried out in a constantly stirred solution. It is shown that on leading oxygen through the solution at a constant rate and increasing the concentration of the potassium cyanide, the velocity of solution in the case of gold increases up to a concentration of 0.3%, and then decreases on further concentration. Ozone and hydrogen peroxide were then used as oxidising agents. It is shown that air containing very little ozone increases the velocity of solution, but if the concentration of the ozone rises to 3—4% the velocity decreases, and at the same time the gold plate becomes coated with a red

layer of oxide. The addition of hydrogen peroxide operates in the same way as ozone. Starting with gold already coated with the oxide layer, and leading air through the solution, the oxide layer slowly disappears, and at the same time the velocity of solution slowly increases. The influence of a number of peroxides is next determined; manganese dioxide and lead peroxide alone have little influence, but when mixed with hydrogen peroxide or ozone the velocity is increased in the same way; the simultaneous action of ozone and hydrogen peroxide increases the velocity of solution in a very notable way. In the case of silver the presence of ozone or hydrogen peroxide causes a rapid increase in the velocity of solution with the rapid evolution of oxygen. In no case is the formation of an oxide layer on the metal noted.

J. F. S.

Connexion Between Electrolytic and Chemical Processes. DAVID REICHSTEIN (*Zeitsch. Elektrochem.*, 1913, 19, 672—676. Compare Andréev, preceding abstract).—The author draws a connexion between the solution of metals as instanced by the solution of gold and silver in potassium cyanide, with the electrolytic solution of passive and active metals by electrolytic processes. This depends on the formation of an oxygen metal alloy as the first stage of the process; thus he formulates the solution of gold in potassium cyanide:



Should the oxygen concentration of the alloy be increased by an increase of the oxidising agent in the solution, a critical oxygen concentration will be reached, and the velocity of the process will decrease the more the concentration of the oxidising agent increases. The appearance of the oxide layer on the gold is therefore not to be regarded as the cause of the retardation of the solution, but a result of the increased oxygen concentration in the metal oxygen alloy.

J. F. S.

Solubility Isotherm at 25° of Lithium Chloride in Mixtures of Alcohol and Water. SANTIAGO PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1913, 11, 422—435).—The solubility of lithium chloride in water falls regularly to about 60 water to 40 alcohol. The curve shows a minimum at 30 water to 70 alcohol. After 20 water to 80 alcohol the solubility falls, but slowly. The composition of the dissolved salt up to 10 water to 90 alcohol is $\text{LiCl}\cdot\text{H}_2\text{O}$, whilst between 90 and 100% alcohol the salt is deposited anhydrous. The saturated pure water and pure alcohol solutions cooled to 0° deposit $\text{LiCl}\cdot\text{H}_2\text{O}$ and $\text{LiCl}\cdot 4\text{C}_2\text{H}_5\text{O}$ respectively.

G. D. L.

Mutual Solubility of the System Benzene-Acetamide. ENRIQUE MOLES and E. JIMENO (*Anal. Fis. Quim.*, 1913, 11, 393—398).—The solubility curve is typical, showing a critical temperature 142.5°.

G. D. L.

Acineta tuberosa. A Study of the Action of Surface Tension in Determining the Distribution of Salts in Living Matter. ARCHIBALD B. MACALLUM (*Proc. Roy. Soc.*, 1913, B, 86, 527—550).—In *Acineta tuberosa*, a protozoan, the potassium can be shown microchemically to be localised in certain situations, and the potassium salt or salts migrate with changes in the tentacles; in retraction, for instance, they pass from the tentacles into the main cell substance. This is due to the action of surface tension. It is suggested that amino-acids are the substances which lower surface tension. The quantity of potassium salt condensed in the surface film of each tentacle appears to be of greater condensation than obtains in sea-water. W. D. H.

The Mechanical Stimulus to Crystallisation. STEWART W. YOUNG and W. J. VAN SICKLEN (*J. Amer. Chem. Soc.*, 1913, 35, 1067—1078).—Further improvements in the apparatus previously used in these investigations (A., 1911, ii, 261, 865) are described, together with the results of new experiments on the supercooling of water. Using a hammer of carbon steel and an anvil of chrome-nickel steel, and starting with freshly polished impact parts, it was found that the impact values showed a rapid decrease as time went on, that is, the sensitiveness of the impact parts gradually increased; after a time the sensitiveness attained a value at which it remained constant for a considerable period, then becoming fluctuating and wholly untrustworthy. It was found that this was due to the impact parts becoming harder, the increase in hardness attaining a maximum after a time. The final fluctuations were possibly due to small fractures being formed, or else to some type of crystallisation being set up. The increased sensitiveness could be destroyed by repolishing.

All the experiments on supercooling were consequently carried out when the maximum sensitiveness had been obtained.

Using a stellite hammer and anvil it was possible to freeze water repeatedly at a temperature slightly under 0.02° below its normal freezing point; thus, if water possesses a metastable limit, it lies at less than 0.02° below the melting point of ice.

The relation between the energy of impact and the supercooling was found to be given by the formula: $(\sqrt{MS} - \Delta)\theta = \text{const.}$, where M is the mass of the hammer in grams, S is the fall distance in centimetres, θ is the supercooling, and Δ is a constant. T. S. P.

The Curie-Wulff Theory of Crystalline Habit. Application to Anisotropic Liquids. GEORGES FRIEDEL (*J. Chim. phys.*, 1913, 11, 478—519. Compare Berthoud, this vol., ii, 305).—Curie's minimum potential theory of crystalline form is not in harmony with the fact that no change is observable in irregular, crystalline fragments immersed in a saturated solution. Moreover, it leads to an impossible definition of melting point, as crystals departing from the equilibrium shape would be more readily melted. The modified theory put forward by Wulff, according to which the rates of growth of crystalline faces are proportional to their capillary

constants, leads to a final condition incompatible with Curie's theory if the original crystal is not in the equilibrium habit.

The Curie-Wulff hypothesis is wholly applicable to liquid crystals if such can exist. Liquid crystals should arrange themselves as perfect polyhedra under the influence of discontinuities in the distribution of surface tension. Lehmann is mistaken in attributing the rounding up of his so-called liquid crystals to the action of surface tension. In the author's view, Lehmann's anisotropic drops are not crystals in the sense that their particles are reticulated or exhibit discontinuities in directional properties. They are merely polarised in the same sense as liquids in a magnetic field, glass under strain, etc., are polarised.

Berthoud's conclusion that specific rates of growth rather than capillary constants determine the form of solid crystals is in accordance with the author's views. It is deduced from the theory of thermodynamic potential that any shape of crystal can be in equilibrium with a limited quantity of saturated solution, but the equilibrium concentration for a given size of crystal depends to some extent on its shape. It is possible that Berthoud's growth constants are related in some way to the capillary constants of the faces.

R. J. C.

Relations of Isomorphism in Organo-metallic Compounds.
IV. **Complementary Investigations.** PAUL PASCAL (*Bull. Soc. chim.*, 1913, [iv], 13, 744—752. Compare A., 1912, i, 524, 739; this vol., ii, 107).—The author has made thermal analyses of binary mixtures made from chlorobenzene, bromobenzene, iodobenzene, and fluorobenzene, the m. p.'s of which are -44.0° , -28.1° , -29.1° , and -40.5° respectively.

Mixtures of chlorobenzene and bromobenzene give a continuous series of mixed crystals, whilst those of chlorobenzene and iodobenzene and of bromobenzene and iodobenzene probably also give a similar series, the freezing-point curves showing, however, minima in these cases. Binary mixtures containing fluorobenzene, on the other hand, yield two series of mixed crystals. According to these results, the elements of the halogen family are divisible into two groups, the first consisting of fluorine only, the second containing chlorine, bromine, and iodine.

The analogy between the cyanogen radicle and the halogens has led the author to examine the freezing-point curve of mixtures of chlorobenzene and cyanobenzene (m. p. -12.1°). In this case, two series of mixed crystals are formed, from which the conclusion is drawn that the radicle is not closely related to the chlorine group.

H. W.

Colloids and the Phase Rule. ERNST HENDRIK BÜCHNER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 60—64).—A theoretical paper, in which the question of the number of phases existent in a colloidal solution is considered. The author advances reasons for regarding the colloidal solution as consisting of one phase only, like the true solutions. This is in opposition to the

view adopted by Pavlov (A., 1910, ii, 1033) and Jonker (A., 1911, ii, 103), who both regard a colloidal solution as made up of two phases. J. F. S.

Theory of the Formation of a Turbidity in Very Highly Disperse Systems. WOLFGANG OSTWALD (*Kolloid. Zeitsch.*, 1913, 13, 121—128).—A theoretical paper, in which the author considers methods of following the change from true solutions through highly disperse solutions to colloidal solutions. The latter solutions exhibit a visible Tyndall cone, but it is shown that probably a great deal of dispersed ultraviolet light accompanies the dispersed visible light. The author considers, therefore, that true solutions which are optically homogeneous when examined in the usual way may show an ultra-violet Tyndall cone if examined photographically. It is also considered possible that associated liquids might be studied in this way. The experiments of Laue (*Bayr. Akad. Wiss.*, 1912, 303) are considered, and the formation of a Röntgen ray Tyndall cone is regarded as likely to lead to valuable information with very highly disperse or even true solutions. J. F. S.

Dependence of the Breaking Strain of Solid Disperse Systems on Temperature. FR. HAUSER (*Kolloid. Zeitsch.*, 1913, 13, 148—150).—The breaking strain of ebonite, wax, colophony, shellac, and mixtures of these substances has been determined at a series of temperatures. The curves obtained fall into two groups: (1) those in which the strain decreases with temperature, and (2) those in which the strain increases to a maximum and then decreases rapidly with increasing temperature. Ebonite, wax, and shellac belong to the first type, and colophony to the second type. The maximum in the case of colophony lies at 30°, which is the temperature at which the coefficient of linear expansion suddenly decreases. The addition of turpentine up to 33% to shellac had a slight lowering influence on the breaking strain, but the influence of a solid substance, such as talc, had no influence on the curve for shellac or any of the turpentine shellac mixtures. On the other hand, colophony was very sensitive to the addition of other substances; thus the addition of 6% of wax changed the curve almost into that for pure wax. The addition of 10% of turpentine lowered the maximum of the curve to below zero. The addition of talc flattened the colophony curve. A mixture of shellac and colophony gave a curve which has the same form as the corresponding curve for cast iron. J. F. S.

Osmotic Pressure of Colloids and its Importance to Biology. BENJAMIN MOORE and HERBERT ELTON ROAF (*Kolloid. Zeitsch.*, 1913, 13, 133—137).—A theoretical paper, in which the osmotic pressure experiments on colloidal substances of Moore, Roaf, and co-workers are summarised. It is shown that many colloidal solutions give rise to an osmotic pressure under conditions which eliminate the action of inorganic impurities. J. F. S.

Separation of Colloidal Solutions. RICHARD ZSIGMONDY (*Kolloid. Zeitsch.*, 1913, 13, 105—112).—The author gives details of methods by which sols of arsenic sulphide, gold, ferric hydroxide, and silicic acid may be separated into two liquid layers. The method consists in mixing the sol with measured quantities of alcohol and ether, and then adding an excess of ether. The remainder of the paper deals with a systematic method of subdividing the subject-matter of colloidal chemistry. J. F. S.

Separation of Colloidal Solutions. WOLFGANG OSTWALD (*Kolloid. Zeitsch.*, 1913, 13, 170—172).—Polemical (compare Ostwald, this vol., ii, 32; Zsigmondy, preceding abstract). It is shown that the cases of separation of colloidal solutions into two layers as studied by Zsigmondy have nothing to do with the typical separation of colloid solutions into two layers, since the cases studied by him are qualitatively identical with the separation of true solutions or even solvents themselves, and show nothing characteristic of colloids. J. F. S.

Mutual Precipitation of Colloidally Dissolved Substances. ANTONI VON GALECKI and M. S. KASTORSKI (*Kolloid. Zeitsch.*, 1913, 13, 143—146).—Biltz (A., 1904, ii, 324) has shown that only oppositely charged sols mutually precipitate one another without the addition of an electrolyte. The present authors have investigated this action, using ferric hydroxide sol, and gold sols prepared respectively by the action of formaldehyde and phosphorus. Measured quantities of the gold sols were added to measured quantities of the ferric hydroxide sol, and the limits determined over which mutual precipitation occurred. Using a 0.1% ferric hydroxide sol, it is shown that 1 mg. of gold, used as a sol prepared from formaldehyde, precipitates 4.98 mg. of ferric oxide, whereas 1 mg. of gold prepared by phosphorus precipitates 18.36 mg. of ferric oxide. In the case of a 0.01% ferric hydroxide sol, the quantities of ferric oxide precipitated are 4.65 mg. and 20.65 mg. respectively for 1 mg. of the two gold sols. The authors consequently draw the conclusion that a colloid phase of finely-divided particles precipitates another colloid phase of opposite charge more energetically than the same colloid consisting of larger particles. J. F. S.

The Influence of the Hydrogen-ion Concentration on Mixtures of Colloids. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1913, 54, 323—329).—A reply to the paper of Landsteiner (this vol., i, 668). The authors do not deny that two oppositely charged amphoteric substances can act on one another over a large range of hydrogen-ion concentrations. They insist on the fact, however, that there is a maximal action at a certain concentration lying between the isoelectric point of the two substances. In order to demonstrate this point experimentally, low dilutions must be chosen, and they illustrate their statement by experiments on the precipitation of gelatin by tannin and on the combination of certain dyes with gelatin. They contend that this

"unspecific" combination of two oppositely charged electrolytes is to be distinguished from a "specific" combination (for example, formation of precipitins), when no sharp optimal point can be ascertained, even in dilute solutions.

S. B. S.

A. Criticism of the Lipoid and Ultra-filter Theories of the Plasma Membrane; the Influence of the Electric Charge of Colloids on Their intra vitam Deposition in the Cell. WILLY RUHLAND (*Biochem. Zeitsch.*, 1913, 54, 59-77).—The author replies to the criticism of Höber and Nast (this vol., ii, 486), who have objected to his ultra-filter theory of the passage of dyes into a cell. It is contended, in the first instance, that the Overton-Meyer lipid theory is insufficient, and numerous examples are quoted of both acid and basic dyes, which are soluble in lipoids (cholesterol in concentrated solution of an organic solvent which does not dissolve the dye), and which are yet incapable of permeating the cell-wall, and of permeating dyes, which are insoluble. It is contended, furthermore, in favour of the ultra-filter theory, that only those dyes in state of high dispersion can penetrate this cell-wall. As criterion for this state of dispersion, the diffusibility through gelatin is employed, and it is shown that those dyes which readily permeate the plasma membrane readily diffuse through the jelly. Attention is called to the fact, however, that a distinction must be made between the permeating capacity and the capacity to be stored in the cell. Basic dyes are readily stored, in that, in coming into contact with acid substances such as tannin, they are precipitated, and thus remain within the cells, and soon become visible. Acid dyes can penetrate without being stored, and a method is described for demonstrating their presence within the cell. The electrical charge on the colloid affects, therefore, their storage capacity, rather than their permeating qualities.

S. B. S.

Starch Jellies. ARTHUR MEYER (*Koll. Chem. Beihefte*, 1913, 5, 1-48).—A very complete investigation of solutions of arrow-root starch and the jellies produced by them has been made. It is shown that solutions produced at 138-140° are not molecular disperse systems, although in many respects they resemble such solutions. These solutions do not exhibit uniform dispersity, and in the swelling of the starch, lumps are produced which even on long heating at 138° do not dissolve. Complete solution only occurs when the starch paste particles are so small and scattered that they can readily pass into solution. The preparation of a colloidal solution of starch at 138-140° consists of two processes: (1) a swelling of the starch granules, and (2) a disintegration of the globules thus formed into tiny drops and crystals. Starch granules are made up of layered spheres of amylose, consisting chiefly of α - and β -amylose. The β -amylose changes on solution of the starch at 100° into drops of a viscous solution of water in amylose, whilst the α -amylose remains undissolved. Thereby each starch granule becomes a globule of porous drops of jelly, which adhere strongly, and the interstices of which are filled by a trichite of α -amylose which can be detected ultramicroscopically. At temperatures of

about 138° the trichite is converted into drops. The drops of the amylose solution of water are very viscous, but on increasing the temperature the viscosity decreases because more water is absorbed, and since this renders them less refractive they are more difficult to detect. The viscosity is so far diminished that at 60–100° the drops flow together to form homogeneous porous drops of irregular form. A colloidal solution of starch which has been prepared by heating at 138° is made up of two phases: (1) a very viscous phase (*Z*), and (2) a phase of low viscosity (*F*). The disperse phase, *Z*, contains particles of varying size, which are due to the varying size of the amylose crystals and the extent to which the drops have united in the preparation. Such an heterogeneous disperse system of amylose never has a greater degree of dispersity than it possesses as soon as prepared at 138°. On cooling such a solution the dispersity decreases, the slower the cooling the greater the decrease. If a dilute solution of amylose is rapidly cooled, the drops of phase *Z* maintain their original size, and only slowly unite with one another to produce conglomerates and an emulsion. If a concentrated solution, in which the drops easily come into contact, is cooled, a thin or a thick jelly is produced, depending on the concentration. With more rapid cooling only small conglomerates of irregular form are produced, whilst with slow cooling larger globules of half-melted drops are produced, from which a jelly globule of amicroscopic drops is formed. All these elements, together with those which have maintained their original form set together in various ways, compose the jelly. The various elements even at 0° possess a definite viscosity, and are not solid. The jellies are consequently porous, and contain the dispersion medium in the pores. The water in the pores is easily movable, whilst that dissolved in the amylose is bound in the sense of a dilute solution, and can consequently exhibit only a small vapour pressure. The concentration of the water in the amylose is smaller the lower the temperature of the jelly. When a jelly is dried at the ordinary temperature the water from the pores evaporates, and the jelly falls together, but maintains its structure. On placing such a dried jelly in water, the form *Z* absorbs a quantity of water corresponding with the temperature, and water enters the pores and again produces the jelly. When a freshly prepared jelly is warmed with water and the temperature constantly increased, the form *Z* takes up more and more water, and its viscosity and refractivity decrease, thereby producing a softer and more transparent jelly. At about 100° the half-melted drops begin to separate from one another, and on further heating the jelly falls into its structural elements. These always have a less total surface than the disperse phase of the freshly prepared solution from which the jelly was produced.

J. F. S.

Colloidal Solutions. II. The System Tannic Acid-Water-Acetic Acid. EMANUELE PATERNO and G. SALINEL (*Kolloid. Zeitsch.*, 1913, 13, 81–88.* Compare this vol., i, 409).—Freezing-point deter-

and *Gazzetta*, 1913, 43, ii, 245–263.

minations have been made of solutions of tannic acid in water, acetic acid, and mixtures of the two solvents. It is shown that the presence of tannic acid does not modify the freezing-point diagram acetic acid-water. A concentration up to 4% of tannic acid in dilute acetic acid brings about a gradual rise in the freezing point of about 0.2° for solutions containing up to 30% acetic acid, and further additions of tannic acid effect no further change in the freezing point. The addition of tannic acid even up to 20% causes no change in the freezing point of a 46.48% acetic acid solution. When the quantity of acetic acid in the mixed solvent exceeds that of the water, the addition of about 10% of tannic acid produces a lowering of the freezing point of about 0.3° . The authors explain these changes by the high absorptive property of the tannic acid, both for water and acetic acid, and they conclude that tannic acid is equally insoluble in both solvents, but forms in both cases colloidal suspensions. J. F. S.

Colloid-chemical Action of Diuretic Salts. MARTIN H. FISCHER and ANNE SYKES (*Kolloid. Zeitsch.*, 1913, 13, 112—121).—The authors have injected a number of salt solutions into the blood of rabbits and rats, and measured the quantity of urine expelled during the following two hours. The salts injected were sodium chloride, magnesium chloride, strontium chloride, calcium chloride, and mixtures of these salts all in $N/4$ -solutions. Further experiments were carried out with various sodium salts, including nitrate, bromide, acetate, phosphate, iodide, and sulphate; magnesium sulphate was also employed. It is shown that the diuretic action of the various salts runs parallel with their dehydrating action on protein colloids, a fact which points to the conclusion that their action in the first place is due to their influence on the substances as a whole, and that they act as diuretics only so far as they supply free water, extracted from the colloids, to the kidneys. The order of the action in increasing degree is sodium, magnesium, strontium, and calcium, and for anions, chloride, bromide, nitrate, iodide, acetate, sulphate, and phosphate. It is shown that the addition of bivalent metals, such as calcium, magnesium, and strontium, has no antagonistic effect on the action of sodium chloride, but, on the other hand, is additive to it. The osmotic theory of the action of diuretic salts is considered in the light of the present experiments. J. F. S.

Phenomena of "Clot" Formations. I. Clotting of Milk. SAMUEL B. SCHRYVER (*Proc. Roy. Soc.*, 1913, B, 86, 460—481).—When solutions of calcium salts and sodium cholate are mixed a clot is formed on heating. In the case of those salts which raise the surface tension of water, the greater the concentration of salt the shorter is the time required for clot formation. Salts which lower the surface tension decrease the clotting time only up to a certain limit of concentration. Above this limit, the clotting time is increased or the clot formation inhibited entirely. The inhibi-

tion of clotting is attributed to the adsorption of simple molecules by the more complex colloids, which are thereby inhibited from aggregation to form a clot. In milk the materials necessary for clot formation pre-exist, but the adsorption of simple molecules from the solution prevents aggregation. The conception is advanced that the ferment clears the surface of the colloid* from adsorbed substances, and allows aggregation to take place.

The solubility in half-saturated lime water is used as a criterion of caseinogen preparations. Products allowed to remain a short time only in contact with acetic acid during preparation give opaque, milky fluids containing 8% of caseinogen. When heated at 37° or allowed to remain with acetic acid a less soluble metacaseinogen is obtained, forming opalescent solutions. Solution of this in sodium hydroxide and precipitation with acetic acid reconverts it into the more soluble form.

The addition of calcium chloride to solutions of caseinogen in sodium hydroxide gives a precipitate only within certain definite limits of concentration of the calcium salt. The addition of rennet to a mixture in which precipitation is inhibited by an excess of the salt immediately causes precipitation. When the optimal amount of calcium salt is present, precipitation may be inhibited by adding milk serum, peptone, or glycine. Rennet only causes precipitation in these cases when too much inhibitor is not present. The final result of the reaction depends on the relative quantities of the various products present in the system. Evidence is quoted to prove that the clot is formed from caseinogen, and not from the calcium salt.

The clot produced by rennet alone is formed from metacaseinogen; that produced by calcium chloride alone is formed from caseinogen. The rennet clot cannot be converted into natural caseinogen. The rennet does not in any way effect proteoclastic digestion in the clot. In milk the clot formation depends on the presence of four series of substances in the system, namely, simple inhibitory substances, colloids, enzymes, and calcium salts.

E. F. A.

Passivity of Metals in the Light of the Theory of Allotropy.

ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 191—192).—The author advances a theory of passivity, which assumes that metals are built up of different kinds of molecules of different reactive power. In such a case the internal equilibrium of the surface layer will be disturbed by chemical action, and on the rapidity with which equilibrium is re-established will depend whether passivity is observed or not.

J. F. S.

Equilibria in Ternary Systems. VIII. FRANS A. H. SCHREINKMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 99—113).—A mathematical paper, in which the composition, entropy, and volume relationships of a liquid, in which two solids are dissolved, with its vapour and the solid phases are considered.

J. F. S.

Equilibria in Certain Organic Systems. NIKOLAI A. PUSCHIN and I. V. GREBENSCHTSCHIKOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 741—745).—The following melting-point diagrams have been traced:

(1) Diphenylamine and *p*-nitroanisole. This consists of two branches meeting in a eutectic point at 20.5°, corresponding with 51.5 mol. % of *p*-nitroanisole. The liquid phases exhibit an orange-red coloration. Solid solutions of appreciable concentration are not formed.

(2) Urethane and diphenylamine. This consists of two straight lines meeting in a eutectic point, 32.2°, which corresponds with 39 mol. % of diphenylamine. No solid solutions of marked concentration are observed.

(3) Urethane and *p*-nitroanisole. The eutectic point here is at 34.2°, whereas Mascarelli (*Gazzetta*, 1909, 39, i, 280) gave 33.2°. Urethane has m. p. 48.3°, that given by Mascarelli being 47.3°. Solid solutions are not formed to an appreciable extent.

(4) *m*-Nitroaniline and naphthalene. The diagram comprises two branches, the eutectic point being 68° and the composition 75 mol. % of naphthalene. Solid solutions were not observed.

T. H. P.

Distribution of a Suspended Substance Throughout Two Liquid Phases, and its Practical Signification. WILLEM REINDERS (*Chem. Weekblad*, 1913, 10, 700—709).—A theoretical investigation of the conditions governing the distribution of a substance in suspension in two immiscible liquids, and a discussion of the bearing of the problem on Elmore's method for the separation of ores, the cleansing action of soap, and the moist preparation of paints.

A. J. W.

The Systems Phosphorus and Cyanogen. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 27—33).—The two systems red phosphorus-yellow phosphorus, cyanogen-paracyanogen are considered. It is shown that both systems are alike and comparable in all respects, and probably belong to the ether-anthraquinone type. It is shown that no connexion can be deduced between yellow phosphorus and violet and red phosphorus, or between cyanogen and paracyanogen, although there obviously must be some connexion, since the phases are respectively convertible into one another.

J. F. S.

The Displacement of the Critical Points of Iron by Addition of Silicon. GEORGES CHARPY and ANDRÉ CORNU (*Compt. rend.*, 1913, 157, 319—322. Compare Vigouroux, this vol., ii, 512).—A study of the variation in the three critical points, a_1 , a_2 , and a_3 , of iron on the addition of increasing amounts of silicon, these points being determined by the rates of cooling of the various alloys. The point a_3 diminishes in intensity as the proportion of silicon increases, whilst passing slightly up the temperature scale, and disappears entirely in alloys containing 1.5% or more of silicon.

The point a_2 passes slowly down the temperature scale as the percentage of silicon increases, but retains its intensity. In alloys containing little carbon, the decrease is 10° to 12° for each 1% of silicon. The point a_1 passes slightly up the temperature scale with increase in silicon, but diminishes in intensity as the carbon becomes converted into graphite, owing to the presence of the silicon, and disappears when the silicon content is above 5%. On account of the opposite natures of the variations of the points a_1 and a_2 , the positions of these two points coincide for an alloy containing 3.16% Si, above which they become inverted. W. G.

The Pseudo-system Methyl Thiocyanate-Methyl Thiocarbimide. ANDREAS SMITS and H. VIXSEBOISE (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 33—39).—It was shown by Walden (A., 1906, ii, 336) that the solution of salts in methyl thiocyanate brought about a lowering of the boiling point, and not raising, as was to be expected. The authors show that this abnormal change is due to the conversion of the thiocyanate into the thiocarbimide, as indicated by $\text{CH}_3\cdot\text{S}\cdot\text{C}\equiv\text{N} \rightarrow \text{CH}_3\cdot\text{N}\cdot\text{C}\equiv\text{S}$. The thiocarbimide has a lower boiling point than the normal ester, which consequently explains the lowering of the boiling point. Quantities of methyl thiocyanate were kept in contact with cadmium iodide for prolonged periods, and then fractionally distilled. It was found that the first portion distilled at 123.6° , and that the temperature continually rose as the distillation proceeded until the last fraction had a boiling point of 136.5° . The boiling point of the *iso*- and normal esters are respectively 119° and 130.5° ; consequently the experiment shows that an internal change occurs in the solvent, and the boiling point is influenced in the normal manner.

J. F. S.

Binary Systems of Thallous Chloride with the Chlorides of Some Bivalent Metals. CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 20—27. Compare this vol., ii, 588).—The paper deals with the thermal analysis of the systems $\text{TlCl}-\text{PbCl}_2$, $\text{TlCl}-\text{SnCl}_2$, $\text{TlCl}-\text{HgCl}_2$, and $\text{TlCl}-\text{CdCl}_2$.

Thallous chloride and lead chloride are completely miscible in the solid state. The curve shows a minimum at about 370° and 40 mol. % of lead chloride.

Thallous chloride and stannous chloride form solid solutions in all proportions. There is a minimum at 185° and 82 mol. % of stannous chloride.

Thallous chloride and mercuric chloride form two compounds. One of these, $\text{TlCl}, \text{HgCl}_2$, melts unchanged at 224° ; the other, probably $4\text{TlCl}, \text{HgCl}_2$, decomposes on fusion, its temperature of formation being 250° . Both form solid solutions with each other and with the simple salts between very wide limits. The eutectic mixture of HgCl_2 and $\text{TlCl}, \text{HgCl}_2$ lies at about 64 mol. % of mercuric chloride and 183° , the limits of existence of saturated solid solutions being 53—76 mol. % of mercuric chloride. The

eutectic mixture of $\text{TiCl}_3\text{HgCl}_2$ corresponds with about 32 mol. % of mercuric chloride and 205° .

Thallous chloride and cadmium chloride form a compound, $\text{TiCl}_3\text{CdCl}_2$, m. p. about 426° . The eutectic mixtures of this compound with the two salts correspond with 27 mol. % of cadmium chloride and 259° , and 66 mol. % of cadmium chloride and 400° respectively.

R. V. S.

The Dissociation of the Molecules into Atoms Considered as one of the Factors of the Velocity of Reaction. E. BRINER (*Compt. rend.*, 1913, 157, 281—284. Compare this vol., ii, 21).—A theoretical discussion of the above question, in which the author considers that the velocity of a reaction is largely controlled by the atoms, arising from the dissociation of the molecules, and on these grounds he explains the inactivity of nitrogen at moderate temperatures, the molecules of nitrogen being very stable, and giving but few free atoms.

W. G.

The Thermal Decomposition of Symmetrical Diarylhydrazines. A Reaction of the First Order. GEORGE O. CURME, jun. (*J. Amer. Chem. Soc.*, 1913, 35, 1143—1173).—The author has investigated the velocity of decomposition of hydrazobenzene, *p*-hydrazotoluene, and *p*-methylhydrazobenzene, the products being mixtures of azobenzene and aniline, azotoluene and toluidine, and benzeneazotoluene, aniline, and toluidine respectively.

From the results the decompositions are reactions of the first order, and the author inclines to the view that a series of changes occurs, namely, $\text{NHR}\cdot\text{NHR} \rightarrow 2\text{NHR} \rightarrow \text{NR}\cdot + \text{NH}_2\text{R}$, concluding with a coupling of the $\text{NR}\cdot$ residues to an azo-compound; the first stage is supposed to be slow in comparison with the others, and so determines the unimolecular nature of the reaction.

The ease of decomposition falls in the order hydrazotoluene ($k=0\cdot00160$ at $110\cdot25^\circ$), methylhydrazobenzene ($k=0\cdot00146$ at $125\cdot30^\circ$), hydrazobenzene ($k=0\cdot00145$ at $140\cdot35^\circ$, $0\cdot00253$ at $145\cdot35^\circ$, $0\cdot00436$ at $150\cdot35^\circ$). This order appears to agree with that of the sensitiveness towards acids, for on treatment with excess of iodine in alcoholic solution for the purpose of estimation of the respective bases by oxidation to the azo-compound, it is found that about 1% of hydrazobenzene, 3% of *p*-methylhydrazobenzene, and 10% of hydrazotoluene undergoes rearrangement on account of the influence of the acid formed; the amount of iodine used up is therefore not strictly equivalent to the quantity of hydrazo-compound applied.

D. F. T.

Catalysis. ISIDOR TRAUBE (*Pflüger's Archiv.*, 1913, 153, 309—322).—A theoretical paper, in which catalysts are discussed; the author considers them in three groups: (a) negative catalysts (bradyatysts), (b) positive catalysts (tachysts), and (c) Eklysts, catalysts which bring about the reaction. In the first two cases it is shown that the substances included under these headings may, under different conditions, act positively or negatively. The pre-

ence and influence of catalysts are considered in the case of disease, and the action of medicines on the catalysts is considered. In the case of the eklysts the author criticises Ostwald's definition of a catalyst, and deduces evidence to show that catalysts can, and do, bring about reactions which could otherwise not occur even very slowly. The examples put forward to support this assertion are of a medical nature.

J. F. S.

A Case of Iron Light Catalysis. H. STAFFORD HATFIELD (*Zeitsch. Elektrochem.*, 1913, 19, 617).—The author shows that the liberation of iodine from a solution of mercuric iodide in potassium iodide in sunlight does not take place if the materials are entirely free from iron. Consequently, he shows that the reaction $2KI + O + Hg = 2KOH + HgI_2$, which takes place in sunlight, is strongly catalysed by iron compounds.

J. F. S.

The Univalent Atom Cannot be a Simple Doublet. MARCEL BRILLOUIN (*Ann. Chim. Phys.*, 1913, [viii], 29, 473—490. Compare this vol., ii, 493).—A mathematical paper, in which the author demonstrates that the conception of a univalent atom as a simple doublet is inadmissible.

H. W.

Some Thermometric and Optical Constants as Functions of the Atomic Weights. WILHELM BILTZ (*Zeitsch. Elektrochem.*, 1913, 19, 613—617).—The author gives very complete curves, which show that the hardness, boiling point, melting point, electric conductivity, light absorption, and index of refraction of the elements are all functions of the atomic weight. The relationships between these various properties are discussed.

J. F. S.

Chemical Papyri of the Third Century (The New Stockholm and the Leyden Papyri). EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1913, 37, 933—934, 962—964, 1002—1004, 1014—1015).—An account of a chemical papyrus discovered at Thebes in 1828, and now preserved at Stockholm. This papyrus amplifies, in a most fortunate manner, the Leyden papyrus, since whilst the latter deals chiefly with the noble metals, the former deals chiefly with precious stones and pearls and with dyeing, in particular purple dyeing; only a small portion relates to the metals.

T. S. P.

Improved Method for the Extraction of Powdery Material. M. KARDOS and W. SCHILLER (*Chem. Zeit.*, 1913, 37, 920).—A perforated glass tube, sealed at the lower end and funnel-shaped at the upper end, is put down the centre of the powder to be extracted, which is contained in a Soxhlet apparatus. The liquid from the condenser falls into the tube, and then percolates uniformly through the powder, the extraction being completed in a much shorter time than if no tube were present. To prevent the perforations of the tube becoming stopped up by the powder, it is provided with a closely-fitting cloth sheath.

T. S. P.

Jacketted Fractionating Column. HENRI VIGREUX (*Bull. Soc. chim.*, 1913, [iv], 13, 868—869. Compare A., 1904, ii, 611).—The previously-described fractionating column has been improved by slightly increasing its diameter (22—23 mm. instead of 15—16 mm.), which permits the introduction of eight points at each stage instead of four. Further, for liquids of b. p. above 100°, the column is now sealed into a glass jacket at a point just below the side-tube. With this apparatus it is claimed that liquids of high b. p. can be fractionated without overheating even when a long column is used. H. W.

Distillation of Petroleum Distillates Under Normal Pressure. A. SCHELLER (*Chem. Zeit.*, 1913, 37, 917).—The author describes an apparatus for maintaining a constant pressure, for example, normal pressure, during the distillation of petroleum distillates. The pressure is maintained constant by means of a Bunte pressure regulator (compare Bunte, A., 1873, 1103). The necessity for such an apparatus arises from the fact that the relative proportions of the various fractions vary with the pressure. T. S. P.

A Simplified Modification of the Skita Hydrogenation Apparatus. H. HEINRICH FRANCK (*Chem. Zeit.*, 1913, 37, 958).—The author describes a simple apparatus, which can be readily built up from material usually found in a chemical laboratory, for carrying out hydrogenations according to Skita's method. T. S. P.

A Water Pump. HENRI VIGREUX (*Bull. Soc. chim.*, 1913, [iv], 13, 869—870).—The pump consists of a glass tube, 15 cm. long and 7—8 mm. wide, constricted at two points in such a manner that the lower constriction has a slightly greater diameter than the upper one. Between the constrictions a bulb is blown, which is subsequently flattened in such a manner as to bring the narrowed portions of the tube as closely together as possible. A side-tube is blown on to the bulb.

When the position of the constrictions is correctly adjusted, the apparatus is stated to give as good a vacuum as can be obtained with the most complicated pumps, whilst, even when this is not the case, it is still sufficiently powerful to bring about rapid filtration. H. W.

Tube for Emptying a Kipp Apparatus. A. FRIEDMANN (*Chem. Zeit.*, 1913, 37, 929).—Through a two-holed stopper in the top of the apparatus are fitted a siphon tube leading to the bottom, and a right-angled tube which reaches a short way below the stopper. By blowing through the second tube the acid is forced out through the siphon. T. S. P.

A Dilution Colorimeter and the Error of Colorimetric Comparison. ROBERT V. STANFORD (*Zeitsch. physiol. Chem.*, 1913, 87, 159—170).—A form of colorimeter is described and figured.

based on the principle of the dilution of a stronger solution of known concentration of the same substance until both solutions have the same colour.

E. F. A.

Simple Ultrafiltration Apparatus. RICHARD ZSIGMONDY (*Zeitsch. angew. Chem.*, 1913, 26, 447—448).—The apparatus consists of three parts, namely, a flanged funnel, perforated disk, and ring; the disk is clamped between the funnel and the ring, the latter forming a receptacle for the liquid to be filtered. The holes of the perforated plate are covered with a filter paper, on which, and covering the whole surface of the plate, is placed a thin collodion film before the several parts of the apparatus are clamped together. With this apparatus, and using a vacuum pump, it is possible to filter colloidal solutions, such as colloidal solutions of gold and iron oxide, very quickly. The apparatus is also of great value in the estimation of gelatinous precipitates.

W. H. G.

Application of Ultrafiltration Apparatus. HEINRICH BECHHOLD (*Zeitsch. angew. Chem.*, 1913, 26, 472).—The apparatus described by Zsigmondy (compare preceding abstract) permits of filtration under a pressure of only one atmosphere. In cases where higher pressures must be employed, the apparatus described by the author previously (compare A., 1908, ii, 24) is suitable.

W. H. G.

Lecture Experiments with Rare Gases. GEORG GEHLOFF (*Physikal. Zeitsch.*, 1913, 19, 838—841).—Six lecture experiments are described to demonstrate (1) the absorptive property of strongly cooled cocoanut charcoal, (2) the preparation of helium from the air, (3) the presence of the rare gases in the air, (4) preparation of argon from the air, (5) the presence of neon in the air, and (6) the presence of helium in radioactive minerals. The experiments all make use of the absorption of the commoner gases by cocoanut charcoal, and the preparation of argon makes use of molten potassium.

J. F. S.

Inorganic Chemistry.

Apparatus for the Preparation of Hydrogen Bromide. ANTONIO GARCÍA BANÚS (*Anal. Fis. Quim.*, 1913, 11, 363—364).—Bromine is dropped, by means of a tap-funnel, on to molten naphthalene at 40—50° contained in a distilling flask, the side-tube of which is sealed to a U-tube containing a few c.c. of water, potassium bromide, and red phosphorus.

G. D. L.

The Sulphur Set Free in the Action Between Sulphurous Acid and Water. ÉMILE JUNGFLEISCH and LÉON BRUNEL (*Compt. rend.*, 1913, 157, 257—262. Compare this vol., ii, 581).—If the

interaction of sulphurous acid and water takes place at a temperature above the melting point of octahedral sulphur, the sulphur is precipitated in a liquid form, which on cooling crystallises in a form depending on the temperature. At 98–100° the sulphur is precipitated sometimes in masses, crystallised after fusion, sometimes in liquid globules, which slowly crystallise on keeping, the sulphur thus being molten at a temperature below its melting point. This is explained on the grounds that the sulphur is produced in the plastic form, which at 100° is converted into the octahedral form with the development of heat, thus raising the temperature of the mass to above 113°. At lower temperatures the sulphur is precipitated in the plastic form. Diagrams are given showing the appearance of the sulphur as precipitated under different conditions.

W. G.

Sulphur, Selenium, and Tellurium. ERNST BECKMANN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 886–894).—Cryoscopic measurements on solutions of naphthalene, diphenyl, aniline, quinoline, etc., in sulphur gave a value of 213 for the freezing-point constant, from which the latent heat of fusion is calculated to be 14.1 cal. Utilising the results of Smith and Holmes (A., 1903, ii, 284), the molecule of amorphous sulphur is then found to be S_{8-12} ; that is, it is probably S_8 . From various considerations the author comes to the conclusion that the molecule S_8 is dark brown, and hence he gives an explanation of the colour assumed by molten sulphur at different temperatures. The explanation involves the assumption of the formation of a complex between crystalline sulphur (S_8) and amorphous sulphur (S_8).

Boiling-point determinations on solutions of sulphur in liquid chlorine prove the existence of the chloride, S_2Cl_2 . When the light yellow solution of this compound is allowed to assume room temperature in a sealed tube, it becomes dark brown after a few hours, owing to the formation of the chloride, SCl_2 .

Cryoscopic and ebullioscopic determinations on solutions of sulphur in bromine do not point to the formation of molecules containing only one atom of sulphur; only the bromide, S_2Br_2 , exists. Similar experiments in iodine solution show that no combination takes place between sulphur and iodine.

Selenium and chlorine give only the monochloride and tetrachloride, of which the latter is the most stable. Ebullioscopic experiments with solutions of selenium in bromine indicate the formation of a mixture of the compounds Se_2Br_2 and $SeBr_2$. In iodine as solvent, selenium exists as the molecule Se_1 to Se_8 , whereas in solvents such as diphenyl and anthraquinone the molecule is Se_8 . The application of various physico-chemical methods does not indicate the formation of any compound between selenium and iodine, and the dissociating effect of iodine on the molecule of selenium still awaits an explanation.

Tellurium dissolves in molten iodine with considerable evolution of heat, and the resulting compounds formed contain 1–2 atoms of tellurium in the molecule.

T. S. P.

The Molecular Weight of Sulphur Trioxide. HENRI GIRAN (*Compt. rend.*, 1913, 157, 375—376).—Assuming the molecular weight of sulphur trioxide as 80, and determining the heats of vaporisation and solidification of liquid sulphur trioxide, the author calculates the constant in de Forcrand's modification of Trouton's law to be 35.8, which is sufficiently close to the value 30, given by de Forcrand, to confirm the exactness of the molecular weight, whilst at the same time pointing to a commencement of polymerisation during liquefaction.

W. G.

The Mechanism of the Formation of Sulphuric Acid in the Lead Chambers. EMIL BRINER and A. KUENE (*Compt. rend.*, 1913, 157, 448—450. Compare this vol., ii, 21).—The authors consider that the formation of sulphuric acid in the lead chambers is due primarily to the direct oxidation of the sulphur dioxide by the atomic oxygen arising from the dissociation of the nitrogen peroxide, the sulphur trioxide formed then combining with the water. They have obtained sulphur trioxide by the interaction of pure dry sulphur dioxide and nitrogen peroxide at temperatures below 60°.

W. G.

Volatility of Sulphuric Acid when Used in Vacuum Drying. H. C. GORE (*J. Biol. Chem.*, 1913, 15, 259—261).—The total loss of sulphuric acid in a Hempel desiccator was 0.00656 milligram per sq. cm. per day. Lime is recommended instead.

W. D. H.

The Chemical Affinities of Nitrogen. GEOFFREY MARTIN (*Chem. News*, 1913, 108, 49—52).—A recapitulation of views already put forward by the author in his book ("Researches on the Affinities of the Elements," 1905), in which he claims priority for expression of the view that from its position in the periodic system nitrogen must be an element possessing strong affinities, and also for clearly indicating on what elements these affinities would be most strongly exerted. Solid curves are given showing how the affinities of the successive elements vary, passing from lithium through boron, etc., on to fluorine.

W. G.

Chemical Reactions at Very Low Pressures. II. The Chemical Removal of Nitrogen in a Tungsten Lamp. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1913, 35, 931—943. Compare this vol., ii, 209).—When a tungsten lamp containing nitrogen at low pressures is run for some time, the nitrogen gradually disappears. Investigation has shown that the disappearance is brought about in three ways, namely: (1) Chemically.—The nitrogen combines with the tungsten vapour to form the brown nitride, WN_2 . (2) Electrochemically.—When an electric discharge passes through nitrogen and a hot tungsten cathode is used, the nitride WN_2 is formed at the cathode. (3) Electrically.—At very low pressures and high voltages there seems to be a reversible removal of limited quantities of nitrogen, in which the nitrogen is driven on to the glass in such form that it can be recovered by heating.

In the present paper the chemical removal is alone considered in detail. From zero pressure up to about 0.001 mm. the rate of removal of the nitrogen is proportional to the product of the rate of evaporation and the pressure of nitrogen. From about 0.003 mm. up to about 1 mm. the rate is directly proportional to the rate of evaporation, and independent of the pressure; above pressures of 2 mm. there is still direct proportionality between the rate of removal and the rate of evaporation, but the latter is materially reduced by the presence of the gas.

The nitride, WN_2 , in thin layers is a clear, brown colour, very different in appearance from finely divided tungsten. It is stable in a vacuum at 400°, but is decomposed at 2400° (abs.). It is decomposed by water, giving ammonia and probably the oxide WO_3 .

The electrochemical removal takes place at much lower temperatures [1900° (abs.)] than the chemical, when potentials much over 40 volts are used in such a way that a perceptible discharge takes place through the gas. The electrical removal occurs at pressures of 0.005 mm. and less, with 250 volts voltage and high filament temperatures; part, at least, of the nitrogen is easily recovered by heating the bulb.

Nitrogen does not, at any temperature, react perceptibly with solid tungsten. The behaviour of nitrogen towards solid tungsten and tungsten vapour is similar to that of oxygen towards platinum and platinum vapour.

The mechanism of the chemical removal is discussed, the discussion being based on the vapour tension of tungsten and the kinetic theory of gases. The equations developed give the vapour pressure of tungsten as 0.080 mm. at the melting point, 3540° (abs.); the boiling point is about 5000° (abs.). The heat of evaporation of tungsten is very high, namely, 218,000–1.87 gram calcs. per gram atom.

T. S. P.

Colloidal Boron. ALEXANDER GUTBIER (*Kolloid. Zeitsch.*, 1913, 13, 137–143. Compare Ageno and Barzetti, A., 1910, ii, 500).—Colloidal solutions of boron have been prepared from boron obtained by the action of magnesium, potassium, and sodium respectively on boron trioxide. The products in each case were extracted with hydrogen chloride and then with water until the aqueous filtrate acquired a decided colour. Then the residues were further extracted with 50–100 c.c. of distilled water and filtered; the coloured filtered solutions constituted the boron sols. From the magnesium preparations two sols were obtained: (1) a relatively unstable sol, and (2) a comparatively stable sol. The former sol had a dark brown to reddish-brown colour, and had a petroleum-like fluorescence in reflected light. This substance could be preserved for three to four weeks in a closed vessel, after which it coagulated rapidly. Attempts to concentrate the solution brought about coagulation, and the addition of electrolytes immediately precipitated the colloid. Dilute nitric acid oxidised the colloid immediately to boric acid, and 7.5% hydrogen peroxide in alkaline solution was immediately decomposed, with the formation of boric

acid. Shaking with charcoal or barium sulphate brought about immediate coagulation, and all attempts to purify the solution by dialysis failed. The solution contained 0.06% of boron, and when coagulated the gel so formed was completely insoluble in water. The relatively stable sol is similar to the foregoing, except that it may be preserved for sixty-four days unchanged and allows of purification by dialysis. Two sols were obtained from the product obtained by the action of potassium; these corresponded in all particulars with the foregoing sols, except that they were somewhat darker in colour. Three sols were obtained from the product of the action of sodium; these differ from the foregoing in their colour, which is deep blue. Two of these are unstable, but a third is stable, and may be dialysed; it coagulates to a deep blue, slimy gel, which is readily soluble in distilled water.

J. F. S.

The Hydrothermal Formation of Silicates. A Review. GEORGE W. MOREY and PAUL NIGGLI (*J. Amer. Chem. Soc.*, 1913, 35, 1086—1130).—In the hydrothermal method of the formation of silicates the components are subjected to the action of water, at temperatures generally near, although often considerably above, the critical temperature of water, in closed bombs, and therefore under the corresponding high pressures developed by such solutions. The authors give a review of all the work which has hitherto been done in connexion with hydrothermal reactions, and append a complete bibliography of the subject.

T. S. P.

Reactions Between Sodium Silicate and Ferric Chloride Solutions. RAPHAEL E. LIESEGANG (*J. pr. Chem.*, 1913, [ii], 88, 358—360. Compare A., 1912, ii, 166).—Under certain conditions the reaction between sodium silicate and ferric chloride may give rise to silicic acid and ferric hydroxide only, no ferric silicate being produced.

When an aqueous solution of sodium silicate (40° Bé.) is covered with a 20% ferric chloride solution in a beaker, the latter solution gradually works its way in a thin layer down the sides of the vessel, and finally completely encloses the silicate solution. Between the two solutions a thin, wrinkled skin is formed, which consists of silicic acid, and is irregularly streaked with ferric hydroxide, enclosed in small folds of the silicic acid membrane.

It is possible that the results obtained by Jordis and others (A., 1908, ii, 291; 1910, ii, 416) may be due to the reaction proceeding to some extent in this direction.

F. B.

Technical Preparation of Baryta. IV. Preparation of Baryta by Electrolysis of Aqueous Solutions of Barium Sulphide. LUIGI MARINO and U. GIULI (*Gazzetta*, 1913, 43, ii, 1—25. Compare Marino, this vol., ii, 592; Marino and Danesi, this vol., ii, 593).—The authors describe a considerable number of experiments undertaken to discover the effect of various alterations in the experimental conditions on this process, which was suggested by Brochet and Ranson (A., 1903, ii, 478). In the work here

recorded, a diaphragm of high resistance is employed in all cases. In certain conditions the yield of barium hydroxide is almost theoretical. The nature of the electrodes is of importance, the best results being obtained with copper. The solution should contain about 20% of barium sulphide, and the electrolysis should be continued for about two-thirds of the time theoretically required for decomposition of the sulphide, using a current density at the anode of 1—3 amperes per sq. dcm. In this case the yields are good, and oxidation products do not amount to more than 4—5%. The barium hydroxide at the anode increases as long as the concentration of the sulphide does not fall below 5%. The quantity of barium hydroxide which can be produced by hydrolysis of the sulphide in concentrated solutions at 70—80° amounts after twenty hours to about 13 grams per litre. The formation of barium hydroxide at the anode in electrolysis is not due to physical phenomena, but to interaction of hydroxyl ions and barium sulphide.

R. V. S.

Action of Various Waters on Lead. HARRI HEAP (*J. Soc. Chem. Ind.*, 1913, 32, 771—775, 811—815, 847—856).—A historical and critical survey of the work already done is first given. In the author's experiments two methods were used: (1) Coils of lead pipes, 10 yards in length, were completely filled with the water under examination, and stoppered so that air was excluded. (2) Pieces of bright lead foil (99.7% Pb) were immersed in water contained in glass cylinders, which were stoppered in such a way that no air remained in the cylinder. Most of the experiments were carried out in a cellar, the temperature of which was fairly constant.

Pure distilled water, free from dissolved gases, exerts but a very slight action on lead; the amount of lead dissolved is so small as to be only just recognisable by the method used (hydrogen sulphide test in Nessler cylinders). Hydrogen, carbon dioxide, oxygen, and air, when dissolved in water, play a part in causing the lead to dissolve, the most potent being oxygen. In the presence of both oxygen and carbon dioxide a reaction takes place which is comparable with that of many natural waters; the lead passes into solution as the hydroxide, and is then precipitated as basic carbonate by the carbon dioxide; the lead has the appearance known as "eroded lead."

Distilled water made slightly acid and then allowed to act on lead produces a liquid which gives no precipitate with carbon dioxide.

Ordinary distilled water behaves very similarly to the distilled water mentioned above, the amount of lead taken into solution being only slightly increased. Distilled waters containing dissolved atmospheric gases attack lead with increased activity as the temperature rises from 5° to 50—60°; at higher temperatures the action diminishes, being the same at 100° as at 5°.

Calcium and sodium phosphates, present in solution, prevent any lead dissolving; ranking next to the phosphates, as regards this

preventive action, are the carbonates and hydrogen carbonates of the alkali and alkaline earth metals. Nitrates attack lead very vigorously, and sulphates, chlorides, and acetates only slightly, with certain exceptions. Ammonium nitrate has a very marked action, ammonium chloride a much less, and ammonium sulphate still less. Aluminium sulphate, and especially calcium hydroxide, dissolve quite large amounts of lead.

The purer natural waters, for example, rain water, exert actions which are comparable with those of ordinary distilled water; lake waters have a much weaker action than distilled water, and differ from the latter in that the amount of lead passing into solution increases continuously with rise in temperature up to the boiling point. The addition of various substances to lake water modifies its action on lead in a manner very similar to that observed with distilled water.

In seeking an explanation of the action of peaty waters on lead, various types of water were subjected to the action of fresh peat. Both distilled water and rain water exerted less action on lead after such treatment than before, although in some cases they showed increased acidity. Soft upland lake water and a hard spring water were rendered more active by such treatment. Certain hard waters, however, especially those in which the hardness is permanent, are not rendered more active by treatment with peat.

T. S. P.

The Cupric Hydroxides and the Heat of Formation of Copper Nitrate; Comparison with Uranyl Nitrate. ROBERT DE FORCRAND (*Compt. rend.*, 1913, 157, 441-444).—A study of the various hydrates of cupric oxide. Peligot's blue hydrate, $\text{CuO} \cdot \text{H}_2\text{O}$, is stable up to 80° for several hours. At 85° it rapidly changes colour to green without loss in weight, but dehydration then commences, and continues progressively; this may be followed by the changes in colour. The author has determined the heat of solution of the various hydrates formed, in the equivalent quantity of dilute nitric acid, and from his results finds that the isomeric change from the blue to the green hydrate is exothermic, and corresponds with 0.261 Cal. From his results, using the figures obtained by Guntz and Martin (*A.*, 1909, ii, 1019) for the heat of solution of anhydrous copper nitrate, the author obtains the value 71.49 Cal. for the heat of formation of this anhydrous salt from its elements and 81.96 Cal. in the dissolved state. These figures are in close accord with the values for uranyl nitrate, starting from uranium dioxide.

W. G.

Preparation and Properties of a Basic Copper Sulphate, $\text{CuSO}_4 \cdot \text{CuO}$. MARIUS EMMANUEL POZZI-ESCOFFÉ (*Bull. Soc. chim.*, 1913, [iv], 13, 816-817).—Basic copper sulphate, $\text{CuSO}_4 \cdot \text{CuO}$, is obtained as a heavy, crystalline, greenish-white precipitate when potassium hydrogen sulphite is added to a hot saturated solution of copper sulphate in commercial formaldehyde which is in contact with a quantity of finely powdered crystals of copper sulphate.

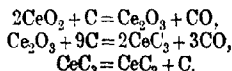
The substance does not possess reducing power. On exposure to moist air, it readily absorbs a molecule of water, forming the green, crystalline compound, $\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_2$. It is insoluble in water, readily soluble in dilute acids. Hot water slowly decomposes it into oxide and sulphate of copper. When heated in a glass tube it becomes yellow, and subsequently melts to a clear, red liquid; it can be maintained at this temperature for a long time without undergoing decomposition.

H. W.

The Critical Temperature of Mercury. ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1913, 35, 1065—1067).—Transparent quartz glass tubes, 7 cm. long and 0.2 mm. in bore, were charged with mercury and then sealed after exhausting to 0.03 mm. pressure. On heating in a muffle, the temperature of which could be kept remarkably uniform, it was observed that the liquid phase disappeared at 1275° . This was not due, however, to the critical temperature being attained, but to the blowing out of the quartz tube, with consequent enlargement of its volume; in no case was the quartz tube ruptured.

Königsberger (A., 1912, ii, 1134) has stated that the critical temperature is in the neighbourhood of 1270° , but in view of the above experiments the author doubts that the critical temperature was ever attained by Königsberger. Theoretical calculations, for example, one based on the relation between the densities of a liquid at different temperatures, as put forward by Thorpe and Rücker (T., 1884, 45, 135), lead the author to the conclusion that the critical temperature for mercury lies above 2600° . T. S. P.

The Products of the Incomplete Reduction of Ceric Oxide. A. DAMIENS (*Compt. rend.*, 1913, 157, 335—338).—The author considers that the oxycarbide of cerium described by Sterba (A., 1902, ii, 399) is not formed by the incomplete reduction of ceric oxide with carbon, but that the reduction takes place in three stages:



The carbide, CeC_3 , is isolated in the form of red crystals, very slowly attacked by water, and yielding acetylenic hydrocarbons under the influence of water.

W. G.

Ultramarine. L. WUNDER (*Chem. Zeit.*, 1913, 37, 1017—1018). A re-statement, for the most part, of results already published (compare this vol., ii, 54). The reduction of ultramarine to a leuco-compound by the action of yellow phosphorus in the presence of carbon tetrachloride is not a direct action of the phosphorus, since a solution of phosphorus in carbon disulphide does not act in the same way. The phosphorus takes chlorine from the carbon tetrachloride, which is at the same time oxidised by the ultramarine to carbonyl chloride: $\text{CCl}_4 + \text{O} = \text{COCl}_2 + \text{Cl}_2$. Sulphur chloride acts in a similar way, gases rich in sulphur dioxide being formed.

Blue ultramarine, when heated with phosphorus trichloride in an autoclave, gives a red product, which becomes blue on heating in the air.

The author does not agree with the view that the blue colour of ultramarine is due to sulphur being present in solid (colloidal) solution (compare *loc. cit.*).

T. S. P.

Preparation of Anhydrous Manganese Iodide. F. DUCELLIEZ (*Bull. Soc. chim.*, 1913, [iv], 13, 815—816).—Anhydrous manganese iodide can be readily obtained by the addition of iodine to finely divided manganese covered with anhydrous ether. A vigorous reaction occurs, which is rendered complete by gentle warming on the water-bath. Excess of iodine and iodide of iron may be removed by washing the product with ether, whilst, if an excess of manganese is employed, it can be separated from the precipitated iodide by washing away the latter in a stream of ether.

When prepared in this manner, manganese iodide is a white substance, which soon becomes discoloured. It is completely soluble in water, and combines energetically with gaseous ammonia.

H. W.

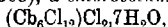
Solubility of Sodium Dichromate in Alcohol. B. REINITZER (*Zeitsch. angew. Chem.*, 1913, 26, 456).—Sodium dichromate is soluble in alcohol to the extent of 5.13 grams of hydrated salt per 100 c.c. of solution at 19.4°; the solution decomposes very rapidly, with the production of acetaldehyde. Ammonium and magnesium dichromates are also soluble in alcohol.

W. H. G.

The Action of Sodium Paratungstate in Fusion on Salts of the Halogen Acids and Oxy-halogen Acids. SIMON BOGHOS KUZIRIAN (*Amer. J. Sci.*, 1913, [iv], 36, 301—304. Compare Gooch and Kuzirian, A., 1911, ii, 657).—In the case of fluorides, chlorides, and bromides, fusion with sodium paratungstate does not lead to complete expulsion of the halogen, since the simple elimination of that element will not leave an oxide to combine with the acidic oxide of the flux. Any expulsion of halogen taking place is due to atmospheric oxygen entering into reaction. Owing to the higher susceptibility of iodides to atmospheric action, fusion with the tungstate gives a quantitative expulsion of iodine. Iodates also give a quantitative loss of iodine (and oxygen), whereas chlorates and bromates are only partly decomposed.

T. S. P.

Haloid Bases of Columbium. HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1913, 35, 1078—1086).—By the reduction of columbium pentachloride with sodium amalgam, using the method and apparatus described by Chapin in the investigation of the haloid bases of tantalum (A., 1910, ii, 303), a *chlorocolumbium chloride*,



is obtained, which is analogous to chlorotantalum chloride (*loc. cit.*). It forms black, shining crystals, which give an olive-green powder, insoluble in cold water, but soluble in hot water

to an olive-green solution. As in chlorotantalum chloride, only two of the chlorines are ionic. When treated with the equivalent quantity of sodium hydroxide, *chlorocolumbium hydroxide*, $(\text{Cb}_6\text{Cl}_{12})(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, is formed as a black, microcrystalline precipitate, and from this the *bromide*, $(\text{Cb}_6\text{Cl}_{12})\text{Br}_2 \cdot 7\text{H}_2\text{O}$, is readily obtained. The hydroxide is soluble in excess of sodium hydroxide, and from the solution excess of concentrated hydrochloric acid precipitates a brown powder, which has a composition corresponding with the formula $\text{Cb}_6\text{Cl}_{14} \cdot 9\text{H}_2\text{O}$. Evidence, which is not yet complete, was obtained that this chloride is probably different in constitution from the green chloride. T. S. P.

The Absorption of Active Hydrogen by Platinum. A. E. FREEMAN (*J. Amer. Chem. Soc.*, 1913, 35, 927—931).—During the course of some experiments in which the pressure in a tungsten incandescent lamp was measured by means of a Hale-Pirani manometer (A., 1912, ii, 230) attached to it, it was found that after the lamp had been lit for some time the manometer readings gave what was apparently a negative pressure. Investigation of the various sources of error which would cause such an abnormality has led the author to give the following explanation: During the burning of the lamp atomic hydrogen is produced by the action of the hot filament on the water-vapour present (compare Langmuir, A., 1912, ii, 1162; this vol., ii, 209); this hydrogen alloys with the platinum of the manometer, increasing its resistance, and thereby causing an error in the calculated pressures. T. S. P.

Removal of Spots on Platinum Utensils Used in Leather Analysis. CRISTO D. MANZOFF (*Ann. Chim. anal.*, 1913, 18, 316—317).—A mixture is made of 1 gram of sodium carbonate and 0.5 gram of borax, and placed on the spot to be cleaned. The whole is heated, first over a bunsen burner and then over the blow-pipe. The fused mass is then removed with hot water; if necessary, the operation is repeated. L. DE K.

Mineralogical Chemistry.

Fractionation of California Petroleum by Diffusion Through Fuller's Earth. J. ELLIOTT GILPIN and P. SCHNEEBERGER (*Amer. Chem. J.*, 1913, 50, 59—100. Compare Gilpin and Cram, A., 1909, i, 1; Gilpin and Bransky, A., 1910, ii, 963).—In continuation of this investigation of the effect on petroleum oils of diffusion through Fuller's earth, it is found that with a specimen D²⁰ 0.912 no fractionation is effected by filtration at the ordinary temperature; on working at 75°, however, a certain fractionation is observable, the

earth tending to retain the sulphur compounds, whilst the issuing oil is not only freer from sulphur, but lighter than the original oil.

Working with a less dense oil (D 0.8890) at the ordinary temperature, results were obtained again indicating a preferential absorption of the heavier constituents of the oil, and at the same time of nitrogen compounds present in the original oil.

When paraffin oil to which benzene has been added is made to diffuse through a tube of fuller's earth, there occurs selective absorption of the benzene.

The important factor in determining the extent to which certain ingredients of an oil will be removed, is not the duration of contact, but the amount of earth with which the oil comes in contact. Indications are obtained supporting the view that the bitumen in the oil investigated was in the form of a colloid, and that the fuller's earth, in exerting the effect of a dialysing septum, caused coagulation and adsorption of the bituminous material with the sulphur and nitrogen compounds and the benzene hydrocarbons, whilst allowing free passage to the paraffin oil.

D. F. T.

Ferriferous Dolomite from the Simplon Tunnel. MARIO DELGROSSO (*Jahrb. Min.*, 1913, ii, Ref. 14; from *Riv. Min. Crist. Ital.*, 1912, 41, 56—64).—The white rhombohedra have a cleavage angle of $73^{\circ}48'$ and D 2.96. They contain a few enclosures of liquid carbon dioxide. The following analysis corresponds with the formula $4\text{CaCO}_3, 3\text{MgCO}_3, (\text{Fe}, \text{Mn})\text{CO}_3$:

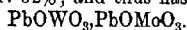
CaO.	MgO.	FeO.	MnO.	CO ₂	Total.
28.78	15.69	9.38	0.26	46.18	100.24

L. J. S.

Some Segregates of Platiniferous Chromite in the Ural Dunites. LOUIS DUPARC and SANTIAGO PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1913, 11, 367—374).—Analyses of the chromites show proportions of olivine varying from 2.40 to 5.12%. The associated platinum metal has 64.65—81.94% of platinum, together with iron, 8.93—15.16%, osmium, rhodium, iridium, and ruthenium.

G. D. L.

"Chillagite," a New Mineral. A. T. ULLMANN (*J. Roy. Soc. New South Wales*, 1912, 46, 186).—The mineral was found in Christmas Gift North Mine, Chillagoe, associated with cerussite in a gossan formation, some of the crystals being studded with small crystals of pure cerussite. The crystallisation appears to be tetragonal; the form is tabular, and the diaphaneity translucent. The mineral is lamellar and straw- or lemon-yellow, sometimes brown, in colour. Hardness 3.5; D 7.5. It contains PbO, 54.25%; WO₃, 28.22%; MoO₃, 17.52%; and thus has the formula



H. W.

Solid Solution in Minerals: Composition of Amorphous Minerals as Illustrated by Chrysocolla. HARRY W. FOOTE and WALTER M. BRADLEY (*Amer. J. Sci.*, 1913, [iv], 36, 180—184. Compare this vol., ii, 717).—The tabulated ratios for previously-

published analyses show a considerable range, and only few of them agree with the usually accepted formula, $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$. New analyses are given of homogeneous material from Arizona (anal. I and II) and Montana (anal. III). The material was selected under the microscope, as it was found that heavy liquids (potassium mercuric iodide solution and acetylene tetrabromide) had some action on the mineral:

	SiO ₂	CuO.	H ₂ O.	Al ₂ O ₃ .	CaO.	Total.	Ratios.		
I.	38.14	36.74	18.73	5.66	0.90	100.17	SiO ₂ :	CuO :	H ₂ O :
II.	38.32	39.98	19.87	0.98	0.78	99.92	1.36 :	1.00 :	2.25 :
III.	50.45	37.94	11.11	—	—	99.50	1.26 :	1.00 :	2.19 :
							1.75 :	1.00 :	1.99 :

These analyses also lead to no definite formula, and the conclusion is drawn that chrysocolla represents a solid solution of copper oxide, silica, and water.

L. J. S.

Mordenite from Tyrol and the Faroe Islands. STANISLAUS J. THUEUR (*Jahrb. Min.*, 1913, ii, *Ref.* 33; from *C. R. Soc. Sci. Varsovie*, 1912, 5, 76—79).—Mordenite from the Seiser Alpe, Tyrol, has the form of rose-coloured needles with an oblique extinction of $7-8^\circ$; analysis I corresponds with the formula $\text{RAl}_2\text{Si}_9\text{O}_{22} \cdot 6\text{H}_2\text{O}$. Fibrous, silky, colourless material from Osterö, Faroe Islands, gave II and III; the difference here is attributed to the presence of enclosed fibrous silica in the material analysed:

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	H_2O	Total
I.	66.86	12.13	0.03	3.86	0.17	0.67	2.41	13.87	100.00
II.	78.70	7.22	—	1.99	—	0.30	2.08	9.71	100.00
III.	74.34	8.84	trace	2.18	—	0.43	2.74	12.05	100.58

L. J. S.

Baueritisation. O. DREIHRODT (*Jahrb. Min.*, 1913, ii, *Ref.* 24—26; from *Diss., Leipzig*, 1912, 39—47).—The natural or artificial process of the bleaching of biotite and its alteration to an end-product consisting mainly of hydrated silica ("bauerite") has been called baueritisation by F. Rinne (*Ber. sächs. Ges. Wiss.*, 1911, 63, 445). Biotite from Brevig, Norway (anal. I, D 3.0417), was digested in water charged with carbon dioxide for five weeks at 30° ; it was then found to be slightly altered in colour, and to have the composition given under II. Digested with concentrated hydrochloric acid for six hours at $80-85^\circ$, the biotite is completely bleached, and the residue has the composition III. D 2.3484. Bleaching is also effected by dilute sulphuric acid in eight hours at the ordinary temperature; the residue has the composition IV, D 2.3488:

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	MnO	Na_2O	K_2O	H_2O	Total
I.	35.05	1.95	16.18	8.34	24.56	3.67	trace	1.00	2.41	5.09	2.36	100.61
II.	39.02	2.23	15.46	10.39	18.74	1.89	—	0.62	1.37	4.50	2.64	100.68
III.	91.85	—	1.01	—	0.45	—	—	—	—	—	7.34	100.65
IV.	85.10	—	1.06	—	0.36	—	—	—	—	—	12.99	99.51

The amount of water present in the residual bauerite is variable, depending on the temperature and on the method of drying.

L. J. S.

Pyroxmangite, a New Member of the Pyroxene Group, and its alteration Product, Skemmatite. WILLIAM E. FORD and WALTER M. BRADLEY (*Amer. J. Sci.*, 1913, [iv], 36, 169—174).—These minerals were found four-and-a-half miles east of Iva, Anderson Co., South Carolina. Pyroxmangite occurs as brown cleavage masses with a cleavage angle of $91^{\circ}50'$, hardness $5\frac{1}{2}$ —6, and D 3.80; the optical characters suggest triclinic symmetry. In composition (anal. I, agreeing with $R^{\#}\text{SiO}_3$) the mineral differs from the manganese pyroxenes, schefférite and rhodonite; and it is regarded as a new triclinic member of the pyroxene group:

	SiO_2	MnO.	O.	FeO.	Fe_2O_3	Al_2O_3	CaO.	H_2O .	Total.
I.	47.14	20.63	—	28.34	—	2.38	1.88	0.33	100.70
II.	—	31.84	6.53	—	43.95	1.96	—	15.56	99.84

A black alteration product of the pyroxmangite has a metallic lustre and a dark chocolate-brown streak; hardness, $5\frac{1}{2}$ —6. It is soluble in hydrochloric acid, and analysis II corresponds with the formula $3\text{MnO}_2, 2\text{Fe}_2\text{O}_3, 6\text{H}_2\text{O}$. This appears to differ from previously-described oxides of manganese and iron, and it is provisionally named skemmatite.

L. J. S.

Two Vanadiferous Ægirites from Libby, Montana. ESPER S. LARSEN and W. F. HUNT (*Amer. J. Sci.*, 1913, [iv], 36, 289—296).—The two pyroxenes described were collected in the Rainy Creek mining district, about seven miles N.E. of Libby, Lincoln County, Montana. The one (A) is an ægirite, and the other (B) an ægirite-augite, and they occur in veins associated with quartz, calcite, microcline, sulphides, and other minerals. The ægirite contains nearly 4% of V_2O_5 , but otherwise its chemical composition is that of ordinary ægirite, with which also its crystal measurements are in close agreement. It is deep brown in colour, and its optical properties differ from ordinary ægirite in the lower index of refraction, weaker birefringence, smaller extinction angle and larger axial angle. The ægirite-augite was found only in fibrous aggregates; it contains nearly 3% of V_2O_5 , and its optical properties are not greatly different from those of ordinary ægirite-augite:

	SiO_2	TiO_2	Fe_2O_3	V_2O_5	Al_2O_3	CaO.	MgO.	FeO.
A.	51.91	0.91	21.79	3.98	0.38	5.53	3.08	1.48
B.	53.32	0.38	12.38	2.86	1.40	12.18	7.01	3.70

	MnO.	Na_2O .	K_2O .	Cr_2O_3 .	S.	CO_2 .	$\text{H}_2\text{O} - \text{H}_2\text{O} +$.
A.	0.58	10.46	0.22	—	0.13	trace	0.06
B.	0.45	6.26	0.26	trace	—	—	0.07

T. S. P.

Meteoric Iron from Paulding County, Georgia. THOMAS L. WATSON (*Amer. J. Sci.*, 1913, [iv], 36, 165—168).—The date of find

and exact locality of this iron are not known. It is mostly rusted away, and only 134 grams of fresh iron now remain. This shows a coarse octahedrite structure. Analyses by W. M. Thornton, jun., of (I) the fresh iron, and (II) of the oxidised portion. In the latter the chlorine is unusually high; another determination gave: Cl, 1.99; H₂O at 110°, 3.34%:

Fe.	Ni.	Co.	Cu.	P.	Cl.	S.	Si.	C.	Total.	Sp. gr.
I. 93.26	6.34	0.50	trace	0.23	0.01	nil	nil	—	100.34	7.886
Fe ₂ O ₃ .	FeO.	NiO.	CoO.	CuO.	SiO ₂ .	P ₂ O ₅ .	Cl.	H ₂ O at 110°.	H ₂ O over 110°.	Total.
II. 36.12	41.26	6.67	0.48	trace	0.26	0.48	2.21	2.77	9.23	99.38

L. J. S.

Analysis of the Gases Spontaneously Evolved from the Spring of Alange. FAUSTINO DÍAZ DE RADA (*Anal. Fis. Quim.*, 1913, 11, 364—367).—The gas contains carbon dioxide, 8.09; oxygen, 6.59; nitrogen and rare gases, 85.32%. The rare gases in two determinations amounted to 1.102 and 1.89% respectively, and consisted of 1.51% of helium and neon and 98.49% of argon, with traces of krypton and xenon.

G. D. L.

A Gas Efflux Rich in Helium. E. CZARÓ and L. LAUTENSCHLAGER (*Chem. Zeit.*, 1913, 37, 936).—The gas issuing from the thermal springs of Wildbad (würtemberg. Schwarzwald) is found to contain 2.79% CO₂, 94.94% N, 1.56% A, and 0.71% He, that is, 2.27% of the rare gases. This result agrees with the previous measurements of Kayser in 1895.

T. S. P.

Manganese in Drinking and Mineral Waters. F. JADIN and A. ASTRUC (*Compt. rend.*, 1913, 157, 338—339).—The authors have determined the amounts of manganese present in a number of samples of drinking and mineral waters from different sources. The majority of the drinking waters show no sign of manganese, whilst the mineral waters from Vichy and Boulou contain it in amounts varying from 0.09 to 0.20 mg. per litre.

W. G.

Analytical Chemistry.

Criticism of a Recent Contribution to the Theory of Indicators. ARTHUR G. A. MILLER (*Chem. News*, 1913, 108, 73—74).—A criticism of views put forward by Waddell (this vol., ii, 522) explanatory of the behaviour of methyl-orange towards weak acids and phenolphthalein towards weak bases. In his arguments the author supports the present views on the behaviour of indicators

(compare Tizard, A., 1912, ii, 598). He has shown that dry hydrogen chloride passed into a solution of methyl-orange in absolute alcohol immediately turns it red, thus refuting another of Waddell's statements.

W. G.

Improvement in Gravimetric Analysis. Ignitions² of Precipitates. GEORGES RAY (*Ann. Chim. anal.*, 1913, 18, 306—309).

—Cylindrical tubes with round bottom and furnished with a small spout, made of fused quartz, and holding 45—85 c.c. are recommended for precipitation, washing, ignition, and weighing in analytical work. The tubes and contents are centrifugalsed for a few minutes in a suitable machine at the rate of 2000—2500 revolutions per minute. In order to assist the drying of the precipitate, this may be centrifugalsed finally with a little absolute alcohol.

L. DE K.

Convenient Device for Analytical Ignitions. EDWARD D. CAMPBELL (*J. Ind. Eng. Chem.*, 1913, 5, 675—677).—A piece of apparatus which serves as a support for crucibles is described. It consists of a fire-clay cylinder, 7.5 cm. internal diameter and 10 cm. high; slits are provided in the upper end, so that the triangle carrying the crucible may be arranged at about one-half the height of the cylinder. The cylinder is wrapped round with asbestos sheeting, and its lower end is secured to an asbestos board, the centre of which is pierced with a hole of such diameter as will admit the tube of a Meker burner. The apparatus is particularly suitable for the conversion of calcium carbonate into calcium oxide, etc.

W. P. S.

The Use of Benzoic Acid as a Standard Material. E. R. WEAVER (*J. Amer. Chem. Soc.*, 1913, 35, 1309—1311).—Benzoic acid absorbs traces of moisture on exposure to the air. Before the pure substance is used as an acidimetric standard (compare Morey, A., 1912, ii, 986) it should be fused at a temperature not higher than 130°. If fusion takes place at 150—160°, small quantities of a brown, resinous substance are formed; this impurity is also formed at lower temperatures, even at temperatures below the melting point, if the benzoic acid is subjected to prolonged heating. The fused product should be quite colourless.

• The test for traces of moisture in benzoic acid was made by dissolving the latter in anhydrous ethyl acetate, shaking the solution with calcium carbide, and then decanting it into an ammoniacal solution of cuprous chloride. The formation of a precipitate of copper acetylide indicated the presence of moisture in the benzoic acid; the delicacy of the test was such that 0.07% of moisture could be detected.

T. S. P.

Determination of Hydrogen, Nitrogen, and Methane in Gas by Combustion in a Quartz Tube. MATHERS and IRA E. LEE (*Chem. News*, 1913, 108, —82).—A description of a new form of combustion apparatus for the estimation of mixtures of hydrogen,

nitrogen, and methane. The authors replace the standard combustion pipette by a narrow quartz tube, filled with scrap platinum, and heated by a flat-flame bunsen burner. The gas residues mixed with oxygen are passed through this tube at a suitable rate, and the issuing gases are collected in a gas burette and their volumes measured. Care must be taken to make due corrections for all temperature changes, and also for the carbon dioxide which remains in the quartz tube after the combustion.

W. G.

A Macro- and Micro-chemical Method for Estimation of Chlorine in the Blood. H. ROGÉE and C. FRITSCH (*Biochem. Zeitsch.*, 1913, 54, 53—58).—The proteins are precipitated from the blood by the method of Michaelis and Rona, namely, the diluted blood is mixed with a colloidal iron preparation and magnesium sulphate is then added, the iron precipitate carrying down all the proteins. In the filtrate the chlorine is estimated by titration with silver nitrate in the presence of potassium chromate. The dialysed iron preparation contains a little chlorine; hence a blank analysis must be made. The microchemical method can be carried out with 1 c.c. of blood, and correspondingly small amounts of reagents. In this case $N/25$ -silver nitrate is used for titration.

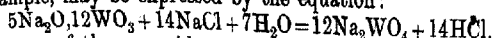
S. B. S.

An Electrochemical Indicator for Oxidising Agents. ERIC K. RIDEAL and ULICK R. EVANS (*Analyst*, 1913, 38, 353—363).—The apparatus, which is intended more in particular for the detection of free chlorine or hypochlorites in treated effluents, consists of a copper tube 3.5 cm. long and 4 mm. internal diameter. Within this, running axially through it, is a platinum rod 1 mm. in diameter, which is insulated at the two ends from the copper tube by ebonite caps. Liquid is allowed to enter the tubes at the lower end at the rate of 230 c.c. per minute (temp. 13°) and to flow out at the top. The copper and platinum are joined to the two poles of a sensitive current-detector of high resistance; the instrument used by the authors had a resistance of 200 ohms, and registered 0.000004 ampere per degree. No visible deflexion of the pointer over the dial is noticed unless the meter contains free chlorine or hypochlorite, even in cases when these cannot be any more detected by the chemical methods, such as the potassium iodide-starch test.

L. DE K.

The Use of Sodium Paratungstate and the Blowpipe Flame in the Estimation of the Acid Radicles of Chlorides, Chlorates, Perchlorates, Bromides, Bromates, and Fluorides. SIMON BOCHOS KUZIRIAN (*Amer. J. Sci.*, 1913, [iv], 36, 305—312).—The author has shown (compare this vol., ii, 685) that the action of fused sodium paratungstate on fluorides, chlorides, bromides, chlorates, and bromates under ordinary atmospheric conditions leads to only partial expulsion of the halogens. He has now found that if the fusion takes place in the presence of superheated steam,

a quantitative reaction takes place, which, in the case of chlorides, for example, may be expressed by the equation:



In the case of the oxy-acids, oxygen is also expelled. The method of using the superheated steam is to apply the blowpipe flame, which contains steam as a product of reaction, directly to the surface of the fused mass. The time necessary for the reaction to become complete is comparatively short, being only five to eight minutes, when 0.2—0.3 gram of the halogen compound is used.

The sodium paratungstate, of which 3 grams are used, is easily prepared by fusing sodium tungstate with an equal weight of tungsten trioxide; it is readily fusible, not volatile under the conditions of experiment, and can easily be kept dry in a desiccator containing sulphuric acid.

T. S. P.

Reaction of the Iodine Ion. RICCARDO CIUSA and ALFREDO TERNI (*Gazzetta*, 1913, 43, ii, 86—90).—The production of oxydimercur-ammonium iodide, which is the basis of Nesler's reaction, can also be used for the detection of iodine. A solution containing 10 grams of mercuric nitrate, 50 c.c. of water, 5 c.c. of nitric acid, and 60 c.c. of concentrated ammonium hydroxide forms the most sensitive reagent for the iodine ion, giving a coloration with potassium iodide at concentrations less than 1×10^{-6} . Chlorides give a white precipitate (of the double salt of the type $\text{Hg}_2\text{NCl} \cdot 3\text{NH}_4\text{Cl}$), which does not interfere with the detection of iodides. Bromides give a white precipitate (probably of analogous composition), which changes spontaneously into the bright yellow substance, Hg_2NBr . The behaviour of a solution containing bromides and iodides towards the reagent depends on their relative amounts, but after boiling it is possible in most cases to recognise the orange-red coloration due to the iodide.

R. V. S.

Estimation of Total Sulphur in Antimonium Sulphuratum. FRANK HARRIS ALCOCK (*Pharm. J.*, 1913, 91, 213).—The addition of sodium potassium tartrate in the oxidation of antimonium sulphuratum keeps the antimony in solution, and a clear liquid is obtained in which the resulting sulphuric acid may be estimated in the usual manner. When the oxidation is completed, the nitric acid may be expelled by evaporation with hydrochloric acid before the sulphuric acid is precipitated as barium sulphate, and it is advisable to add a small amount of potassium nitrate at the commencement of the oxidation in order to fix the sulphuric acid as it is formed.

W. P. S.

Estimation of Small Quantities of Hydrogen Sulphide in Waters. LUDWIG WILHELM WINKLER (*Zeitsch. anal. Chem.*, 1913, 52, 641—645).—The testing is preferably done at the source of supply. The water is allowed to flow through a 100 c.c. flask until the first portions, which have been affected by contact with the air, have been completely expelled. At the bottom of the flask, now quite filled, is introduced by means of a long-stem pipette 5 c.c. of

the lead reagent. In a 200 c.c. beaker are now put 100 c.c. of pure water and 5 c.c. of the lead reagent; the darkened contents of the flask are transferred to a similar beaker, and to the colourless mixture is then added drop by drop from a burette a solution of sodium sulphide until the required colour is obtained. The calculation will be readily understood.

The lead reagent is prepared by dissolving 10 grams of Rochelle salt, 10 grams of ammonium chloride, and 0.1 gram of lead acetate in 5% ammonia up to 100 c.c. The sodium sulphide solution is prepared by dissolving an accurate weight (about 0.1 gram) of the pure crystallised salt in 100 c.c. of a strong solution of sodium nitrate containing a few drops of ammonia just before use.

The presence of iron does not interfere with the test provided some Rochelle salt is first added to the sample. Coloured waters cause trouble.

L. DE K.

Estimation of Thiosulphates in the Presence of Sulphites. A. A. BESSON (*Chem. Zeit.*, 1913, 37, 926).—In one portion of the amount of solution the sulphite and hydrogen sulphite is estimated according to Bosshard and Grob's method (this vol., ii, 428). To another portion of the solution are added 25 c.c. of *N*/10-alkali, 20 c.c. of hydrogen peroxide solution (5 c.c. of Merck's "perhydrol" diluted to 100 c.c.), after which it is heated for ten minutes on the water-bath, and then, after cooling, the excess of alkali determined by titration with standard acid, using methyl-orange as indicator (compare A., 1907, ii, 811). Only the hydrogen sulphite and the thiosulphate require alkali during the oxidation, as shown by the equations: $\text{NaHSO}_3 + \text{NaOH} + \text{H}_2\text{O}_2 = \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$; $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH} + 4\text{H}_2\text{O}_2 = 2\text{Na}_2\text{SO}_4 + 5\text{H}_2\text{O}$. The amount of alkali used up by the hydrogen sulphite is known, and consequently the amount of thiosulphate present is readily calculated.

T. S. P.

Determination of Ammonia and Nitrogen. A. J. VAN EYNDHOVEN (*Zeitsch. angew. Chem.*, 1913, 26, 472. Compare Knublauch, this vol., ii, 789).—The forms of apparatus usually described for use in the determination of ammonia in gas-works products are needlessly complicated. Perfectly accurate results are obtained by distilling the ammonia from a flask fitted with a stopper through which passes a thistle funnel and a glass tube, bent twice at right angles, and dipping into standard acid. W. H. G.

The Diphenylamine Reaction for Nitric Acid. D. J. DE JONG (*Pharm. Weekblad.*, 1913, 50, 992—993).—A criticism of the method of Tillmans and Sutthoff (A., 1911, ii, 767) for the detection of nitric acid. The author finds that the more concentrated the diphenylamine solution is, the less sensitive is the reagent.

A. J. W.

A Rapid Method for the Estimation of Phosphorus in Steel. HARIPADA BHATTACHARYA (*J. Soc. Chem. Ind.*, 1913, 32, 738—739).—The yellow ammonium phosphomolybdate precipitate obtained

from steel in the usual manner is washed with 1% nitric acid until free from iron, and the nitric acid then eliminated by washing with a 1% solution of potassium nitrate. The filter and precipitate are transferred bodily to a 200 c.c. flask, 20 c.c. of *N*/10-sodium hydroxide solution and 2 drops of phenolphthalein are added, and the excess of alkali titrated with *N*/10-hydrochloric acid. The reaction taking place is expressed by the equation: $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 + 24\text{NaOH} = (\text{NH}_4)_3\text{PO}_4 + 12\text{Na}_2\text{MoO}_4 + 12\text{H}_2\text{O}$. The results are accurate.

T. S. P.

Mocagno's Method for the Volumetric Estimation of Phosphorus in Steel. HENRYK WDOWISZEWSKI (*Chem. Zeit.*, 1913, 37, 1069—1071).—A modification of the original method. Two grams of steel turnings are placed in a 300 c.c. flask and dissolved in 30 c.c. of nitric acid (D 1.2) at the boiling temperature, when 5 c.c. of permanganate solution (40 grams per litre) are added. After boiling until a separation of manganese peroxide takes place, this is redissolved by adding 1 c.c. of a saturated solution of ammonium oxalate. When cold, 5 c.c. of concentrated ammonia are added, when a dark brown jelly is formed; 25 c.c. of nitric acid are now added, and the liquid is heated almost to boiling until the iron precipitate has redissolved. Fifty c.c. of the usual molybdate solution are added, and after thorough shaking for five minutes the flask is kept for ten minutes in a warm place. The yellow precipitate is then collected and washed first with dilute (1%) nitric acid and then three times with cold water to remove the free acid. The funnel is replaced in the flask, and the contents dissolved by means of a 4% ammonium solution. The filter is washed with hot water until the filtrate amounts to about 30 c.c. To the solution are then added 80—100 c.c. of dilute sulphuric acid (1:4), 10 grams of pure zinc are introduced, and the whole heated on a sand-bath for forty-five to fifty minutes short of boiling, although the reduction is generally complete within thirty-five minutes. The reduced, green, and quite clear solution is now poured into a known volume (10—15 c.c.) of standard permanganate, the flask and zinc are washed with hot dilute sulphuric acid (1:10), and the excess of permanganate is titrated with oxalic acid (1 c.c.=1 c.c. permanganate). In the author's experiments the strength of the permanganate was such that 1 c.c. represented 0.00818% of phosphorus.

L. DE K.

Estimation of Phosphorus in Steels Containing Vanadium. JOHN R. CAIN and F. H. TUCKER (*J. Ind. Eng. Chem.*, 1913, 5, 647—650).—Phosphoric acid may be precipitated as phosphomolybdate in the presence of vanadium salts, provided that the vanadium is reduced previously to the quadrivalent state. This reduction is best attained by the action of ferrous sulphate and sulphur dioxide, and, if care is taken to prevent the temperature rising above 15° during the precipitation of the phosphomolybdate in the presence of nitric acid, the excess of ferrous sulphate is not oxidised by this acid. The details of the method are as follows:

VOL. CIV, ii.

From 1' to 2 grams of the steel are dissolved in 100 c.c. of nitric acid (D 1.135), the solution is oxidised by boiling with a slight excess of permanganate, sulphur dioxide is then added, and, after cooling, 40 c.c. of ammonia (D 0.96) are added. The mixture is now cooled to 15°, 5 c.c. of a saturated ferrous sulphate solution and 5 drops of concentrated sulphurous acid are added, followed by 40 c.c. of molybdate reagent. The whole is stirred or shaken for ten minutes, and the precipitate is then collected, washed, and titrated by the alkalimetric method. Nickel, copper, chromium, molybdenum, or aluminium when present in the steel do not interfere with the method, but tungsten, titanium, arsenic, tin, etc., must be removed.

W. P. S.

Estimation of Phosphoric Acid in Basic Slag. MAX POPP (*Zeitsch. angew. Chem.*, 1913, 26, 480).—The author states that the "citrate process" is a compensation method, the precipitation of the phosphoric acid not being complete, but loss is prevented by the co-precipitation of calcium triphosphate. The magnesium mixture may also deposit some magnesium oxide, so that the composition of the precipitate is no longer true ammonium magnesium phosphate.

The Lorenz method when applied to basic slags gives results which are a trifle too low.

L. DE K.

Estimation of the Phosphoric Acid Soluble in Citric Acid in Basic Slag. MAX POPP (*Chem. Zeit.*, 1913, 37, 1085—1087. Compare this vol., ii, 336).—In order to oxidise the hydrogen sulphide it is found better to employ 1 c.c. of 3% hydrogen peroxide than 10 c.c. of 0.3% solution. It is occasionally necessary to add more than 1 c.c. The hydrogen peroxide is most conveniently measured by means of the burette employed by Gerber for measuring the amyl alcohol in estimating milk fat.

N. H. J. M.

Estimation of the Phosphoric Acid, Soluble in Citric Acid, in Basic Slag by the Citrate Method and by Lorenz's Method. HUGO NEUBAUER (*Landw. Versuchs-Stat.*, 1913, 82, 465—475).—Lorenz's method gives correct results, and is not affected by the citric acid. The citrate method gives high results, even when iron citrate is employed, owing chiefly to the precipitation of some mg. of calcium as tricalcium phosphate, which is not compensated for by incomplete precipitation of the phosphoric acid.

The error in the citrate method, due to the lime, is greater in the case of the citrate-soluble phosphoric acid in basic slag than in estimating the water-soluble phosphoric acid in superphosphates.

N. H. J. M.

Quantitative Analysis of Mineral Phosphates and Ashes by the Carbon Tetrachloride Method. PAUL JANASCH and ROBERT LEISTE (*J. pr. Chem.*, 1913, [ii], 88, 273—292).—Having shown previously that metallic phosphates are completely decomposed and

the phosphoric acid quantitatively volatilised by heating them with quartz powder in a stream of carbon tetrachloride, the authors have now applied this method of decomposition to the analysis of mineral phosphates. Full details of the analysis of triphylite, vivianite, pyromorphite, and fluorapatite are given. F. B.

A Simple Method for the Determination of Carbon in Organic Materials. EDWIN BERT HART and K. J. WOO (*J. Amer. Chem. Soc.*, 1913, 35, 1056—1061).—The method depends on the oxidation of the carbon and fixation of the carbon dioxide by the use of sodium peroxide, the oxidation being effected in an ordinary iron, nickel, or, less satisfactorily, porcelain crucible. Six grams of sodium peroxide and 0.1 gram to 2 grams of the substance for analysis are well mixed in the crucible, which is then fitted with a tight lid; the larger limit to the quantity of substance is for ordinary soils, whilst the lower limit is for peat soils and organic substances containing more than 40% of carbon. To prevent the absorption of carbon dioxide from the heating flame, the crucible is enclosed in a larger iron or nickel crucible of 120 c.c. capacity, which is also covered, and as a further precautionary measure is fitted in a hole in a piece of asbestos board. Gentle heating is then applied, and should be continued for three to five minutes after the first vigorous action has subsided. When cool, the contents of the crucible are transferred to a flask by carbon dioxide, free water, and distilled with 25% sulphuric acid, the evolved carbon dioxide being collected in a measured volume of sodium hydroxide solution of known strength (compare Browser, A., 1912, ii, 995; Brubaker, this vol., ii, 433).

The method gives accurate results, and is especially suitable for routine carbon determinations, for example, in soils, but it can also be applied to the analysis of organic substances. D. F. T.

Modified Platinichloride Method for the Estimation of Potassium. W. B. HICKS (*J. Ind. Eng. Chem.*, 1913, 5, 650—653).

—The following method is applicable to the estimation of potassium in the presence of all other salts with the exception of those of ammonium, cesium, and rubidium; organic compounds must also be absent. The solution containing the potassium is acidified with hydrochloric acid and evaporated with an excess of chloroplatinic acid solution to a syrupy consistence. After cooling, 80% alcohol is added, and the precipitate is collected on a filter and washed with alcohol in the usual way. The precipitate is then dissolved in hot water, the solution is acidified with 1 c.c. of concentrated hydrochloric acid, and a quantity of magnesium ribbon sufficient to effect complete reduction of the platinum is added. The excess of magnesium is dissolved by the addition of hydrochloric acid, and the flocculent platinum is collected, washed, ignited, and weighed.

W. P. S.

Estimation of Lithium in Mineral Waters. LUDWIG WILHELM WINKLER (*Zeitsch. anal. Chem.*, 1913, 52, 628—640).—Mainly on account of hygienic reasons, isobutyl alcohol is recommended

instead of amyl alcohol for the separation of lithium chloride from the chlorides of potassium and sodium; 10 c.c. of this solvent dissolves only 0.5 mg. of alkali compounds (weighed as sulphate).

Lithium has a tendency to precipitate when the water is mixed with sodium hydroxide and carbonate. Hence, the water, if its hardness exceeds 100° (German), should be suitably diluted; even then a double precipitation of the calcium, etc., is advisable.

Sulphates are decomposed in the acidified filtrate by cautious addition of barium chloride. In order to concentrate the lithium it is advisable to evaporate the filtrate to a small bulk, and to precipitate most of the alkali chlorides by adding a large excess of alcohol. After removing the last traces of calcium, magnesium, barium, and aluminium by means of a successive treatment with alkali and ammonia, and then again completely expelling the latter by evaporation with a little alkali, the solution is acidified with hydrochloric acid and evaporated to dryness. After heating at 120° the mass is powdered and exhausted with isobutyl alcohol, using in all 10 c.c. As, however, a portion of the lithium chloride is retained in the residue, it is necessary to again dissolve this in a little water and a drop of hydrochloric acid; the residue on evaporation is then treated as before; a third treatment may even be advisable. The author prefers weighing the three results separately. Finally, the lithium chloride is converted into sulphate by ignition with about 0.05 gram of ammonium sulphate. Allowance is then made for the traces of alkali sulphates.

L. DE K.

Detection of Small Quantities of Silver. G. MALATESTA and ETTORE DI NOLA (*Boll. chim. Farm.*, 1913, 52, 533-535).—Meneghini's reaction (compare A., 1912, ii, 390) can be employed as a sensitive test for silver. When a solution of a silver salt is treated with a solution of a chromium salt and then rendered alkaline with potassium or sodium hydroxide, a black precipitate (Ag_2O) is produced, and the liquid becomes yellow from formation of chromate. The reaction is more sensitive than precipitation of silver chloride, for 0.000005 gram of silver per c.c. is recognisable.

R. V. S.

Volumetric Estimation of Calcium. THEODOR DÖRING (*Zeitsch. angew. Chem.*, 1913, 26, 478-480).—The time honoured process of titrating calcium by precipitation as oxalate and titrating this, after thorough washing, with standard permanganate in the presence of dilute sulphuric acid at 70°, gives excellent results when the liquid contains at most 0.2 gram of the metal. With larger quantities much manganous sulphate accumulates during the titration, and this has an injurious effect. Moreover, large precipitates require much washing, and calcium oxalate is not absolutely insoluble in pure water.

When applying the "residue method" (titrating the excess of the oxalic acid added) the calcium oxalate which includes ammonium oxalate, should be thoroughly washed with hot water, and the washings added to the main filtrate. This is then made up

to a definite bulk, and an aliquot part of it taken for the titration. This modification, however, renders the process more complicated, so the first method is to be preferred.

L. DE K.

Observations and Proposals Regarding the Chemical Testing of Plaster. ALFREDO CAVAZZI (*Gazzetta*, 1913, 43, ii, 71—86).—The author discusses methods which have been proposed for this purpose, and describes modifications of them.

R. V. S.

Colour Reactions of the Alkaline Earths with Tannic and Gallic Acids and Pyrogallol. OMER SCHEWKET (*Biochem. Zeitsch.*, 1913, 54, 285—290).—A number of colour reactions given by the above-mentioned phenolic substances (called by the author oxygallols) with salts of the alkaline earths in presence of alkalis are described and tabulated. Certain of these are applicable to qualitative analysis. Calcium may be detected in the presence of barium and strontium by the addition of a few crystals of pyrogallol to a 2% solution of the mixture, followed by the addition of a few drops of alkali; an intense violet colour is thereby produced. If the solution containing alkaline earths is diluted with half its volume of alcohol, and a few drops first of 1% gallic acid and then alkali hydroxide solution are added, a pink precipitate and then gradually a blue coloration of the fluid ensue. The former indicates the presence of calcium. After separation of calcium by the ordinary alkaline reactions, strontium can be detected in the presence of barium by the following reaction. The salts are converted into sulphates, and then treated with water, in which strontium sulphate is sufficiently soluble, to yield the colour test. This consists in the addition of a little solid tannin, followed by the addition of a few drops of alkali hydroxide solution. A bright green colour forms in the presence of strontium.

S. B. S.

Separation of the Alkaline Earth Metals. J. L. M. VAN DER TORN VAN DEN BOS (*Chem. Weekblad.*, 1913, 10, 665—666. Compare A., 1911, ii, 228; this vol., ii, 153).—In the author's method the presence of ammonium acetate must be avoided, since it increases the solubility of the strontium chromate. The weighing of the chromates of barium and strontium can be avoided by dissolving them in cold hydrochloric acid, adding potassium iodide, and titrating the liberated iodine with thiosulphate.

A. J. W.

Estimation of Small Quantities of Lead Obtained During Extraction with Lead-glazed Pans. P. A. MEERBURG (*Chem. Weekblad.*, 1913, 10, 752—758).—A comparative investigation of the methods for estimating lead described in *Centr. Gezondh. Raad Maandblad.*, 1908, 155, and *Arb. Kais. Ges. Amte*, 1910, 33, II, 203. The results obtained by the first method were found to be inaccurate.

A. J. W.

Estimation of Copper with Sodium Hypophosphite. JOS. HANUS (*Zeitsch. anal. Chem.*, 1913, 52, 616—618).—A criticism of Windisch's paper (this vol., ii, 247). The author has made a sub-

stantial improvement in the estimation of copper by means of hypophosphite. A sensible source of error is caused by the oxidation of the precipitated copper by atmospheric oxygen in presence of free acid. The author now neutralises this acid by means of normal alkali, with phenolphthalein as indicator; no copper is then redissolved, even after a long interval before collecting it.

The process, however, although very convenient, cannot lay claim to great accuracy, and is not suitable when other metals have to be estimated in the filtrate.

L. DE K.

Estimation of Copper by means of Hypophosphorous Acid. RICHARD WINDISCH (*Zeitsch. anal. Chem.*, 1913, 52, 619—628).—The author states that the amount of copper found becomes less when the precipitate is left in contact with the acid liquid for a considerable time before filtering. Filtration without delay is therefore advisable.

The copper obtained proved to be of great purity. L. DE K.

The Use of Tantalum Electrodes for the Electro-analytical Estimation of Copper and Zinc. GUSTAV WEGELIN (*Chem. Zeit.*, 1913, 37, 989).—In contradistinction to Brunck (*A.*, 1912, ii, 1128), the author finds that tantalum cathodes give unsatisfactory results in the estimation of copper from copper sulphate solutions at 70°, and of zinc from either alkali zinc oxide or sodium acetate electrolytes. The results for copper are satisfactory at room temperature.

T. S. P.

Analysis of Bauxites. ERNEST MARTIN (*Ann. Chim. anal.*, 1913, 18, 297—305).—The author objects to the processes based on fusion as these cause an undesirable accumulation of alkali salts in the filtrate. One gram of the mineral is heated in a flask with 15 c.c. of nitro-hydrochloric acid (equal volumes) and 30 c.c. of dilute sulphuric acid (1:1 by volume) until dense, white fumes appear and solid sulphates begin to separate. The residue is then dissolved in 50 c.c. of water. The silica is collected, but before weighing it must be purified by fusion with at most 0.5 gram of potassium pyrosulphate; the aqueous solution is then united with the main filtrate, which is now made up to 500 c.c.

In 200 c.c. of this the joint oxides of iron, titanium, and aluminium are precipitated by ammonia; the filtrate contains only calcium. In another portion of the original liquid the iron and titanium are estimated by the usual gravimetric, volumetric, or colorimetric (titanium) processes; alumina is taken by difference. A table is appended, giving the composition of a large number of French bauxites.

L. DE K.

Colorimetric Estimation of Small Quantities of Manganese in Water. E. SCHWALTER (*Zeitsch. Natur. Genussm.*, 1913, 26, 104—108).—In the estimation of manganese by converting it into permanganate by means of nitric acid and ammonium persulphate it is necessary to remove previously any chloride which may be present. This may be done by the addition of silver nitrate, but

the turbidity produced interferes with the subsequent colorimetric estimation; at the same time, the hydrochloric acid cannot be expelled by heating the water with sulphuric acid and persulphate. Silver nitrate, however, appears to enter into the reaction taking place when the permanganate is formed, and the author recommends the following procedure: 100 c.c. of the water are treated with 10 c.c. of nitric acid, and evaporated; the dry residue is moistened with 10 c.c. of nitric acid, again evaporated, then dissolved in 5 c.c. of nitric acid and 10 c.c. of water, and filtered. The insoluble residue is washed with water, and the filtrate, measuring about 35 c.c., is heated to boiling after the addition of 5 c.c. of nitric acid and 1 gram of ammonium persulphate. Ten drops of a 5% silver nitrate solution are now added, and the mixture is boiled for ninety seconds after the first appearance of a pink coloration. The solution is then cooled, and the coloration compared with *N*/100-potassium permanganate solution. (NOTE.—If 100 c.c. of *N*/100-potassium permanganate solution be diluted to 110 c.c., each c.c. will correspond with 0.0001 gram of manganese.)

W. P. S.

Analysis of Ferro-titanium. A. R. SCOTT (*Chem. News*, 1918, 108, 52—53).—The finely-powdered alloy (0.25 gram) is fused with potassium hydrogen sulphate (10 grams) until all grit has disappeared. The residue is cooled and extracted with warm dilute sulphuric acid, and filtered. The residue is again fused, extracted, and filtered, the two filtrates being mixed.

The residue is ignited and weighed, the silica removed with hydrofluoric acid, and the residue again weighed. From this the ferric oxide is extracted with hydrochloric acid and precipitated with ammonia, any remaining residue being titanium oxide.

The original combined filtrates are boiled, made just alkaline with ammonia, and then just acid with hydrochloric acid; the titanium is precipitated by the addition of sodium thiosulphate, and is collected, ignited, and weighed as the oxide. The filtrate is evaporated to small bulk, oxidised with bromine water, any titanium oxide that may have passed through the filter being filtered off, and the iron and aluminium precipitated by ammonia and weighed as the mixed oxides, in which the iron is estimated by solution in hydrochloric acid, reduction with stannic chloride, and titration with potassium dichromate. The manganese is estimated in the filtrate from the mixed hydroxides by precipitation with bromine and ammonia.

W. G.

Detection of Chromium. ALFREDO TERNI (*Gazzetta*, 1913, 43, ii, 63—65).—When a solution of a chromic salt containing nitric acid is boiled with lead peroxide, oxidation to chromate occurs, and the yellow colour due to this can be recognised even with 0.1 milligram of chromium; or the chromate may be detected with hydrogen peroxide and ether, 0.005 milligram of chromium being then still evident. The test may be used for the examination of the precipitate obtained in the third group of the ordinary analytical scheme.

In this case, if iron is present, the lead chromate may be precipitated by the addition of sodium acetate, or may be detected by means of hydrogen peroxide and ether. When the substance to be analysed contains manganese, permanganic acid is also formed, and masks any yellow coloration; in this case, addition of hydrochloric acid to the warm liquid decomposes the permanganic acid, and any yellow coloration can then be seen.

Chromic salts in acid solution can also be oxidised by means of potassium permanganate, but the reaction in this case is not so sensitive. Volhard's reaction for manganese (oxidation to permanganic acid by means of lead peroxide) is not trustworthy when traces of manganese are accompanied by considerable quantities of chromium.

R. V. S.

The Quantitative Separation of Chromium and Aluminium. Analysis of Chromite FRANÇOIS BOURION and A. DESHAYES (*Compt. rend.*, 1913, 157, 287—289).—The method employed for the separation of the oxides of chromium and iron, by chlorination with a mixture of sulphur dichloride and chlorine, and treatment of the chlorides by water, the anhydrous chromic chloride being insoluble (compare this vol., ii, 626), can be used for the separation of the oxides of aluminium and chromium. This method is applicable for a complete analysis of chromite. The powdered mineral is first heated gradually to a red heat with mercuric sulphate, and then, thus prepared, it is chlorinated. The residue in the tube contains the unattacked silica and the chlorides of magnesium and calcium. Of the volatile chlorides, the chromic chloride alone is insoluble in water, and can be filtered off, the iron and aluminium being estimated in the filtrate by the usual methods. W. G.

A Delicate Test for Molybdenum. A. KOMAROWSKY (*Chem. Zeit.*, 1913, 37, 957).—The colour test for molybdenum by means of the formation of ammonium permolybdate (Melikoff, A., 1912, ii, 693) is exceedingly delicate; it is sensitive to 0.006 mg. of molybdenum.

T. S. P.

Quantitative Precipitation of Tungstic Acid by Aromatic Amines. ERWIN KAFKA (*Zeitsch. anal. Chem.*, 1913, 52, 601—606).—To 50 c.c. of sodium tungstate (= about 0.25 gram of the solid salt) are added, respectively, 15 c.c. of ψ -cumidine, 10 c.c. of tetramethyldiaminodiphenylmethane, or 10 c.c. of tetramethyldiaminobenzophenone reagent. When the precipitate has completely settled, it is collected and washed with water containing 5 c.c. of the reagent per 100 c.c., and then ignited to tungstic oxide.

The reagents are, respectively, prepared as follows: 5 grams of ψ -cumidine are mixed with 10 c.c. of water, dissolved by means of 5 c.c. of hydrochloric acid, and diluted to 100 c.c.; 6 grams of tetramethyldiaminodiphenylmethane are dissolved in 4 c.c. of hydrochloric acid and diluted to 100 c.c.; 7.5 grams of tetramethyldiaminobenzophenone are dissolved in 10 c.c. of hydrochloric acid, and diluted to 100 c.c.

The precipitates obtained with the two last reagents have the compositions $\text{WO}_3 \cdot \text{C}_{17}\text{H}_{22}\text{N}_2$ and $2\text{WO}_3 \cdot 3\text{C}_{17}\text{H}_{20}\text{ON}_2$ respectively.

L. DE K.

Solution and Oxidation of Tin in Dilute Nitric Acid. CURT BUNGE (*Pharm. Zentr.-h.*, 1913, 54, 845—846).—When assaying commercial tin, the author finds that this may be readily oxidised and dissolved by heating 2 grams of the sample free from grease with 30 c.c. of dilute nitric acid and a drop of a concentrated solution of mercuric chloride. On evaporation on the water-bath a transient coagulation of stannic nitrate is noticed. On boiling the dry residue with dilute nitric acid, insoluble stannic acid is again obtained.

L. DE K.

Detection of Gold and Platinum. GIUSEPPE MALATESTA and ETTORE DI NOLA (*Boll. Chim. Farm.*, 1913, 52, 461—463).—The reagent employed contains 1 gram of benzidine, 10 c.c. of acetic acid, and 50 c.c. of water. It yields, with traces of a gold salt solution, an intense blue coloration, which becomes violet. In the presence of free acetic acid the coloration is green, passing into blue when excess of benzidine is added. The blue coloration is distinct when the gold solution contains only 0.0000035 gram of gold per c.c. The same reagent, when treated with a solution of a platinum salt, yields in the course of ten minutes a blue, flocculent precipitate; the reaction is perceptible with a solution containing only 0.0000125 gram of platinum per c.c. A solution of a ferric salt, when treated with benzidine acetate, gives a blue coloration, which is stable only in the presence of excess of benzidine. When gold or platinum is being tested for, however, the absence of iron may be ensured by a previous treatment of the material with dilute acid.

R. V. S.

Some Anomalies Observed in the Assay of Platinum Ores from the Ural. MAX WUNDER and V. THÜRINGER (*Ann. Chim. Phys.*, 1913, [viii], 30, 164—168).—Certain anomalies observed when assaying the "Ural ore" have led Holtz (this vol., ii, 144) to the conclusion that an unidentified metal is present in the material. This appears improbable to the authors. The difference in weight between the portion of the "blacks" dissolved by nitric acid (1:1) and the weight of palladium + copper found by Holtz is attributed to the presence of the excess of zinc used in the reduction. The yellow colour of the filtrate from the copper thiocyanate and the dark precipitate formed by the addition of zinc to it are also encountered with solutions containing rhodium. Holtz deduces the absence of rhodium from the fact that the metal, after solution by melting with potassium hydrogen sulphate, yields a brownish-red mass, which does not give a white turbidity with water. The authors do not regard this as characteristic of the metal, and insist on the dependence in behaviour of the sulphate on the temperature at which the fusion has been performed.

H. W.

Separation of Palladium from Gold, Platinum, Rhodium, and Iridium. Application of Dimethylglyoxime. MAX WUNDER and V. THÜRMER (*Zeitsch. anal. Chem.*, 1913, 52, 660—664).—*Gold from Palladium.*—Both metals are precipitated on boiling the solution containing a little hydrochloric acid with excess of dimethylglyoxime; the other members of the platinum group (except platinum itself) are not precipitated. After ignition and redissolving the metals in *aqua regia* the gold may be recovered as metal by warming with ammonium oxalate; the separation of the gold is promoted by adding some dilute sulphuric acid; from the filtrate the palladium may then be again recovered by heating with dimethylglyoxime after first neutralising the bulk of the acid with ammonia. The palladium compound is first ignited in the air, then in a current of hydrogen, and allowed to cool in a current of carbon dioxide. *Platinum from Palladium.*—The platinum is separated by saturating the concentrated solution with ammonium chloride, washing with ammonium chloride, and finally igniting the precipitate. From the filtrate the palladium is then recovered by means of dimethylglyoxime. *Palladium from Rhodium.*—The palladium is removed by means of dimethylglyoxime. After destroying the excess of this reagent by means of hydrochloric acid and sodium chlorate, the rhodium may be precipitated by means of metallic magnesium, the last traces of which are removed by means of 5% sulphuric acid. The metal is then ignited in a current of hydrogen, and allowed to cool in a current of carbon dioxide. *Palladium from Iridium.*—The same process as for rhodium is used; the complete destruction of the excess of dimethylglyoxime is of great importance in this case. L. DE K.

Method of Estimation of Pure Caoutchouc in the Crude Product. RAYMOND MARQUIS and F. HEIM (*Bull. Soc. chim.*, 1913, [iv], 13, 862—866).—When a solution of pure caoutchouc (1 gram) in chloroform (100 c.c.) is violently agitated with pure sulphuric acid (8 grams) during three to five minutes, a clear, yellow, mobile solution is obtained, from which the caoutchouc is quantitatively precipitated as a white, amorphous powder when the solution is poured into alcohol (200 c.c.). The precipitate has the further advantage of being readily filtered, washed, and dried.

The application of this method to the estimation of pure caoutchouc in artificial mixtures of this substance with varying amounts of rubber resin gives satisfactory results when the quantity of acid employed is increased to ten times the weight of the caoutchouc. Nevertheless, in view of the extremely variable character of the resin present even in similar samples of crude caoutchouc from the same locality and also because the presence of resin frequently retards the filtration very considerably, the authors are led to recommend the de-resinification of samples by means of acetone previous to their assay. H. W.

Alcoholometry. ALFRED FRANCIS JOSEPH and W. N. RAE (*J. Soc. Chem. Ind.*, 1913, 32, 856—857).—In the determination

of the strength of alcoholic liquids by the distillation method the authors have investigated the effect of the temperature of the condenser water on the results obtained, and also the probable errors caused by the use of Sikes' hydrometer. It is found that condensation of the distillate is equally efficient when the temperature of the condenser water varies between 15.5° and 49°. Using the ordinary density tables, a large error is caused when the density is measured with the Sikes' hydrometer; at 37.7° the error may amount to as much as 6% of proof spirit. A great improvement is made if the tables compiled by C. H. Bedford are used in conjunction with Oertling's glass Sikes' hydrometer, or even with the ordinary brass instrument, which, however, is not so good. T. S. P.

New Colour Reactions for Di- and Tri-phenols. OMER SCHEWKEK (*Biochem. Zeitsch.*, 1913, 54, 282—284).—Catechol, when treated with a few drops of 1% iodine solution in potassium iodide and then, after dilution, with a few drops of 5% sodium hydroxide solution, yields immediately a bright green colour. The immediate production of this colour distinguishes catechol from resorcinol. Pyrogallol under the same conditions yields a fugitive violet colour. This substance, when its aqueous solution is diluted with half the volume of alcohol and a few drops of a solution of alkali hydroxides, gradually gives a violet colour similar to that of permanganate solutions. This test serves to distinguish pyrogallol from phloroglucinol. When a hot dilute aqueous solution of the latter substance is treated with a few drops of 0.5% iodine solution in potassium iodide, the iodine is decolorised. On addition of a few drops of alkali solution, a bright, brown coloration is formed, which on heating becomes violet. Phloroglucinol in alkaline solutions yields, on treatment with hydrogen peroxide, a very stable, bluish-violet coloration, which gradually changes into red and then yellow on addition of acids, and is restored again on addition of alkalis.

S. B. S.

The Differentiation of Vegetable and Animal Oils. J. MARCUSSEON and H. SCHILLING (*Chem. Zeit.*, 1913, 37, 1001—1002).—The authors make use of the fact that cholesterol and phytosterol form characteristic, sparingly soluble compounds with digitonin (compare Windaus, A., 1909, i, 172). Combination of the precipitation of these compounds with Bömer's phytosteryl acetate test gives a simple method for distinguishing between animal and vegetable oils.

Fifty grams of the oil or fat are shaken for fifteen minutes in a separating funnel with 20 c.c. of a 1% alcoholic solution of digitonin. When the emulsion has cleared, the bottom layer of oil is run off, and then the alcoholic upper layer, which contains the flocculent precipitate of the digitonide, is shaken with 50—100 c.c. of ether. After collecting the digitonide it is washed with ether to remove oil, dried, powdered, and again washed with ether to remove the last traces of fat, after which it is heated in a test-tube with

1.5 c.c. of acetic anhydride for half-an-hour. On cooling, the cholesteryl and phytosteryl acetates crystallise out; they are recrystallised once or twice from alcohol, and then the melting points determined, etc., as in the Bömer test. If desired, the acetates may be hydrolysed and the free alcohols obtained.

It is not necessary to saponify fats, or extract the higher alcohols from them, previously to treatment with the digitonin.

T. S. P.

Quantitative Estimation of the Cholesterol Substances in the Presence of One Another. II. Cholesterol. J. LIFSCHÜTZ (*Biochem. Zeitsch.*, 1913, 54, 212—235).—Qualitatively as well as quantitatively, both oxysterol and cholesterol behave similarly towards Liebermann's "cholesterol" reagent, that is, a mixture of acetic anhydride and sulphuric acid. The colours produced by this reaction pass through three stages, namely, a red, a blue, and a green stage. The second (blue) stage is characterised by absorption bands in the yellow, which extend until they include the whole of the orange and the greater part of the green part of the spectrum. The third stage (green) is characterised chiefly by a band in the red between the *B* and *C* lines. It is shown by the author that the bands in the second stage may be most readily obtained if a relatively larger quantity of sulphuric acid is added, whereas the band in the red of the third stage is best obtained if sulphuric acid in smaller quantity (sulphuric acid diluted with ten times its volume of acetic acid) is employed. The bands of either the second or third stage may be employed for quantitative estimation of the combined cholesterol or oxysterol content, the solution under investigation being compared with a solution of known content of either of these substances. For this purpose either the necessary dilutions necessary to bring the bands to disappearance or the spectrometric method already described by the author (*loc. cit.*) for the estimation of oxysterol by the acetic and sulphuric acid reagent in the presence of iron salts, may be employed. By the latter method the oxysterol may be estimated separately, and by the quantitative application of Liebermann's reaction, the total cholesterol and oxysterol may be estimated. Liebermann's reaction is only applicable to the estimation of these substances when they are not combined as esters of the higher fatty acids. In the presence of chloroform, however, as in Burchard's modification of the method, the cholesterol and oxysterol as fatty esters can also be estimated. By estimating the substances by both the Liebermann and the Liebermann-Burchard methods, both the free and combined "cholesterol" substances can be estimated.

S. B. S.

The Action of Sugar Solutions on Glass. J. N. LAIRD (*J. Path. Bact.*, 1913, 18, 32—33).—When sugar solutions are heated in ordinary test-tubes they extract calcium from the glass, and this accelerates the reaction with Fehling's solution. Of five reducing sugars investigated, galactose is the most sensitive to the presence of calcium hydroxide.

W. D. H.

A Source of Error in the Estimation of the Sugar in the Blood of Frogs and Tortoises. ERNST J. LESSER (*Biochem. Zeitsch.*, 1913, 54, 252—255).—When attempts were made to estimate the sugar by Bertrand's method, after precipitation with Michaelis and Rona's colloidal iron hydroxide reagent, no copper reduction took place. When, however, the filtrate from the proteins had been treated with mercuric nitrate before the sugar estimation, a certain amount of cuprous oxide was precipitated. The conclusion is drawn that the blood of these cold-blooded animals contains some substance which retains cuprous oxide in solution.

S. B. S.

Influence of the Alkali of Ordinary Water on Dextrose. H. J. WATERMAN (*Chem. Weekblad*, 1913, 10, 739—742).—The results obtained in the polarimetric estimation of dextrose dissolved in ordinary water containing alkali are much too low. A. J. W.

Estimation of Traces of Dextrose in Urine by the Bertrand Method. ELSE HIRSCHBERG (*Zeitsch. physiol. Chem.*, 1913, 86, 484—493).—Use is made of Oppler's observation (*A.*, 1912, ii, 100) that the addition of alcohol to a sugar determination eliminates the reducing action of the substances which accompany dextrose in urine. To apply the Bertrand permanganate method to the titration of dextrose in urine, the urine was first shaken with charcoal and hydrochloric acid, and diluted. Equal volumes of the diluted urine and alcohol were taken. Quantities of 0.5—0.9% of dextrose were accurately determined; quantities of 0.1—0.5% tended to give slightly low results.

E. F. A.

Estimation of Dextrose in Faecal Matters. L. H. DEJUR (*Ann. Inst. Pasteur*, 1913, 27, 570—576).—Twenty-five grams of the substance are mixed in a flask with 125 c.c. of 96% alcohol, neutralised with acetic acid, and, after the addition of 5 c.c. of 10% acetic acid, the mixture is boiled for fifteen minutes under reflux. The solution is then filtered, and the insoluble residue is extracted twice again with alcohol in the same manner, the residue being finally washed with about 20 c.c. of alcohol. Two c.c. of 10% hydrochloric acid are added to the alcoholic extract, and this is evaporated under reduced pressure to a syrupy consistence. The syrup is dissolved in water, transferred to a 50 c.c. flask, 12 c.c. of mercuric nitrate solution are added, the mixture is neutralised with sodium hydroxide solution, diluted to the mark, and filtered. The filtrate is shaken for forty-five minutes with an excess of zinc dust (about 5 grams), again filtered, and the reducing power of the filtrate is determined.

W. P. S.

Fische's Reaction [for Honey]. J. GERUM (*Zeitsch. Nahr. Genussm.*, 1913, 26, 102—104).—The fact that some samples of genuine honey give an orange or reddish-yellow coloration with this test for invert sugar (*A.*, 1910, ii, 660) is due to the presence of traces of wax substance in the honey. When such a reaction is obtained, a larger quantity of the honey should be extracted with ether, and the

residue obtained on evaporating the ether examined for the presence of beeswax. W. P. S.

Estimation of Oxalic Acid. IW. BUROMSKY (*Centr. Bakt. Par.*, 1913, ii, 38, 506—507).—A reply to Wehmer (this vol., i, 432). Extraction of the fungus with hydrochloric acid was avoided, as it would cause loss of weight.

When the precipitate, obtained by Wehmer's method, contains much calcium phosphate and sulphate it is proposed to titrate with permanganate, as these salts do not readily dissolve in acetic acid after being heated with calcium chloride and ammonia.

N. H. J. M.

[**Estimation of Oxalic Acid.**] C. WEHMER (*Centr. Bakt. Par.*, 1913, ii, 38, 508).—A reply to Buromsky (preceding abstract).

N. H. J. M.

Estimation of Tartaric, Malic, and Succinic Acids in Wines. PAUL DUTOIT and MARCEL DUBOUX (*Bull. Soc. chim.*, 1913, [iv], 13, 832—862).—The authors have previously described a method of volumetric analysis (A., 1910, ii, 342) which is based on the determination of the end-point in a precipitation process by means of conductivity measurements. When successive quantities of a concentrated solution of a precipitant are added to a dilute solution of a precipitable salt and the conductivity after each addition is plotted as a function of the volume of the solution of the precipitant added, two approximately straight line graphs are obtained, the intersection of which corresponds with the point of complete precipitation. The application of this method to the estimation of tartaric, malic, and citric acids in wines is now described.

The use of salts of barium, lead, glucinum, bismuth, cadmium, lanthanum, magnesium, and silver as precipitating agents is discussed, lanthanum nitrate being finally chosen. When, however, this reagent is added to solutions of alkaline salts of tartaric, malic, and succinic acids and the results plotted as above, two straight-line curves are obtained, the inflexion of which only corresponds with the point of complete precipitation, assuming the formation of $\text{La}_2(\text{C}_4\text{H}_4\text{O}_6)_3$ when the experiments are performed with aqueous solutions; with aqueous alcoholic solutions, less reagent (up to 8%) appears to be required, so that it is necessary in practice to standardise the lanthanum nitrate solutions against solutions of sodium tartrate and malate of known concentration.

In order to obtain a solution of the sodium salts of tartaric, malic, and succinic acids suitable for titration from a given wine, the total acidity and sulphates in the latter must first be determined (A., 1908, ii, 781); 100 c.c. of the wine are heated to boiling and treated with exactly that quantity of barium hydroxide (or of a barium salt) which is necessary to precipitate the sulphates and with 1 c.c. *N*-uranium nitrate solution; after several minutes sodium hydroxide is added until the mixture is neutral to litmus, followed by a sufficient volume of aqueous-alcoholic silver nitrate

solution to precipitate tartaric, malic, and succinic acids as silver salts. A large excess of silver nitrate is to be avoided as the presence of an excess of sodium nitrate (subsequently formed) interferes with the delicacy of the titration. After filtration, the precipitate is decomposed by agitation with the necessary volume of *N*-sodium bromide solution, and the solution made up to 200 c.c. with an aqueous alcohol containing 50% alcohol (95%).

In one portion of this solution, the sum, tartaric + malic + succinic acid, is determined by titration with lanthanum nitrate solution. The exact volume of solution to be taken and the volume of 50% alcohol to be added to ensure the complete precipitation of the lanthanum salts of the acids depend on the acidity of the wine. Before titration, the solutions are acidified by 0.5 c.c. *N*/10-acetic acid.

In a second portion of the solution, tartaric and malic acids are estimated together, lanthanum nitrate being again used. Precipitation of lanthanum succinate is avoided by performing the titration in a more strongly acidified solution, which also contains a larger proportion of alcohol, the exact proportion of the various solutions depending, as before, on the acidity of the wine.

The estimation of tartaric acid alone is performed in a still more strongly acidified solution and in the presence of a larger proportion of alcohol. Barium acetate solution is used as a precipitant. The results are only accurate if the proportion of tartaric to malic acid exceeds 3.7. If this is not the case, a suitable known volume of sodium tartrate solution must be added, and the determination repeated.

The method gives accurate results with wines which contain less than 3.4 grams of malic acid per litre, that is, in the great majority of cases. Certain wines, such as those of 1912, contain up to 8 grams of malic acid per litre. For these it is preferable to estimate the tartaric acid as potassium bitartrate, and to subtract the value thus found from the sum of tartaric + malic acid determined by the conductivity method. The determination of succinic acid is also less precise in the presence of much malic acid.

Citric acid, if present, is precipitated in each of the determinations described above. In order, therefore, to apply the method to wines containing this acid, a fourth determination is necessary, which may consist in estimating the tartaric acid either as potassium bitartrate or as calcium racemate.

H. W.

Increased Sensitiveness of Mylius' Reaction for the Detection of Cholic Acid and for Distinguishing it from the True Bile Acids. JULES VILLE (*Bull. Soc. chim.*, 1913, [iv], 13, 866—868).—Mylius (A., 1887, 606) has shown that when a solution of iodine in aqueous potassium iodide is added to an alcoholic solution of cholic acid and the mixture gradually diluted with water, a brown solution results, which deposits the compound $(C_{24}H_{40}O_5I)_2KI \cdot nH_2O$, fine blue needles with reddish-brown reflex. The author finds that the sensitiveness of this reaction may be greatly increased either by the addition of solid sodium chloride

to the reaction mixture or by dissolving the iodine and potassium iodide in a concentrated solution of sodium chloride. In this manner, 0.0005 gram of cholic acid immediately yields a deposit of blue crystals, whilst the presence of 0.0002 gram acid gives an appreciable reaction.

H. W.

Oxidation of Gallic and Tannic Acids in Air in the Presence of Alkalis, and a Colour Reaction for Lead. OMER SCHWEKET (*Bioc. Chem. Zeitsch.*, 1913, 54, 277—284).—If a solution of gallic acid is poured over a solution of alkali, the upper layer is coloured green, and the lowest pink, the intervening layer being yellow. These colours correspond with various stages in the oxidation of the acid. The green colour can be produced by adding a few drops of 10% alkali hydroxide to the gallic acid solution, preferably in presence of alcohol. With excess of alkali, and in presence of air, an orange-red colour is formed. Experiments showing that the formation of these colours represent stages in the oxidation, are given. If to a lead salt solution sufficient sodium hydroxide is added to dissolve the precipitated lead hydroxide, a solution is obtained, which, on addition of a few drops of gallic acid solution, shows on the surface (if the mixture is not shaken) a green zone, and below a carmine-red zone. On shaking, the whole mass becomes carmine red. For this reaction lead must be in excess. Tannin gives the same reaction. If a larger amount of gallic acid is added (1—4 c.c. of a 1% solution to 5 c.c.) a green colour is produced. The production of the red colour is the more delicate test.

A method is also given for the detection of gallic and tannic acids in the presence of one another. The tannic acid is precipitated by caffeine, and in the filtrate the gallic acid can be detected by the following tests: (1) Half the volume of alcohol is poured on to the liquid, and then a few drops of sodium hydroxide solution. A green colour develops in the alcoholic layer. (2) The following reagent can be employed: 5% sodium hydroxide solution, containing 0.2% lead acetate. This is added drop by drop with constant shaking, whereby a green colour is produced, which turns red on addition of acids. (3) The addition of barium chloride, followed by sodium hydroxide, produces a blue precipitate. The tannic acid can be detected in the caffeine precipitate when this is dissolved in alcohol by the following reaction. On addition of a few drops of sodium hydroxide solution a reddish-yellow precipitate is formed, which dissolves in water with a reddish-yellow colour. Gallic acid under the same conditions gives a green solution.

S. B. S.

Application of "Activated" Aluminium to the Estimation of Tannin. ÉMILE KOHN-ABREST (*Ann. Chim. anal.*, 1913, 18, 349—351).—The method depends on the direct precipitation of tannin from its solution by means of aluminium which has been treated with mercuric chloride solution. One hundred c.c. of the tannin solution are brought into contact with a piece of aluminium foil (about 1 mm. in thickness and weighing 3 grams) which has

been immersed for three minutes in a 3% mercuric chloride solution and then washed. About four hours' contact is required to precipitate the tannin completely; if after this time the solution still yields a coloration with ferric chloride, a fresh piece of treated aluminium is introduced. The mixture is then filtered, and an aliquot portion of the filtrate is evaporated. The difference between the weight of the residue obtained and that found on evaporating an equivalent portion of the original tannin solution, gives the weight of the tannin precipitated. A small quantity of aluminium passes into solution, and an allowance may be made for its amount by incinerating the residues and ascertaining the difference between their weights.

W. P. S.

Estimation of Tyrosine. EMIL ABDERHALDEN (*J. Biol. Chem.*, 1913, 15, 357—358).—Polemical. A criticism of Folin and Denis' method. It is stated that tryptophan and other substances give the same colour reaction, and therefore the method is not accurate for the estimation of tyrosine.

W. D. H.

Detection of Formaldehyde in Foods. F. RACHEL (*Pharm. Zentr.-h.*, 1913, 54, 759—761).—Attention is called to some colour reactions recommended by Friesse (*Hyg. Inst.*, Dresden, 1907, 1) for the detection of formaldehyde. On this the author has based the following process for the detection of this preservative in meat, caviare, and fish wares.

The article is acidified with phosphoric acid and heated in a current of steam; 1 or 2 c.c. of the distillate are then mixed with 4 c.c. of milk free from formaldehyde and 10 c.c. of hydrochloric acid (D 1.19), to which has been added 1 drop of nitric acid per 300 c.c. In the presence of formalin a bluish-violet coloration appears; no notice must be taken of any coloration formed after five minutes. In presence of much formaldehyde milk will not give the reaction, so the experiment must be repeated after suitably diluting with pure water.

L. DE K.

A Colour Reaction of Hypochlorites with Methylaniline and Ethylaniline. PAUL NICHOLAS LEECH (*J. Amer. Chem. Soc.*, 1913, 35, 1042—1044).—Contrary to the statement of Hofmann (A., 1874, 807), carefully purified methylaniline gives a navy blue coloration when 1 c.c. of a *N*/100-aqueous solution is treated with a few drops of 6*N*-sodium hydroxide solution and $\frac{1}{4}$ —2 c.c. of half-saturated solution of bleaching powder. The colour begins to appear in approximately twelve seconds, reaches a maximum in about thirty-five seconds, and after a minute or so slowly fades to a yellow, a precipitate of calcium carbonate being simultaneously produced. It is suggested that the reaction may depend on the primary oxidation of the methyl group (compare Meisenheimer, this vol., i, 447).

Ethylaniline gives an analogous but slower reaction, but the blue colour passes through green and dark brown before changing to yellow.

D. F. T.

Estimation of Small Amounts of Caffeine. A Comparison of Methods. P. L. MURRAY (*J. Ind. Eng. Chem.*, 1913, 5, 668—670).—For the estimation of caffeine in substances containing less than 0.5% of the alkaloid, Götter's method (extraction of the moistened sample with chloroform, evaporation of the extract, separation of fat by adding water and filtration, and again extracting the caffeine with chloroform) yields results which are considerably higher than those obtained by Lendrich and Nottbohm's method (*A.*, 1909, ii, 449). The latter method gives concordant results, and the necessity of the permanganate purification as described by the authors of the method is confirmed. W. P. S.

Colorimetric Estimation of Adrenaline in Desiccated Suprarenal Glands. ATHERTON SEIDELL (*J. Biol. Chem.*, 1913, 15, 197—212).—Previous methods were tested and found unsatisfactory. The new method proposed consists in the use of manganese dioxide as the reagent for developing a colour with aqueous adrenaline solutions, or extracts of suprarenal glands. The colour is estimated against standards made by mixing cobalt chloride, gold chloride, and water. W. D. H.

Detection of "Saccharin" in Beer. RENÉ LEDREY (*Ann. Chim. anal.*, 1913, 18, 314).—Beer is allowed to traverse drop by drop a long and narrow column of ether, thus avoiding emulsion and insuring complete extraction of the "saccharin." A modification of Duyk's apparatus (*A.*, 1906, ii, 407) is employed. L. DE K.

New Indican Reaction. ADOLF JOLLES (*Zeitsch. physiol. Chem.*, 1913, 87, 310—312).—Urine containing thymol gives a violet coloration with potassium indoxylsulphate in presence of an oxidising agent in strongly acid solution. The following test for indican is based on this observation. Urine is precipitated with lead acetate, and filtered. A little alcoholic thymol is added to the filtrate, together with strong hydrochloric acid containing ferric chloride and chloroform. The whole is well shaken, when in presence of traces of indican the chloroform is coloured a deep violet. On shaking with water, the colour changes to a yellowish or reddish-brown. *p*- and *o*-Xylenols give a similar violet coloration, which, however, is stable towards both water and alkali. E. F. A.

Detection of Hæmatin in Human Blood Serum. OTTO SCHUMM (*Zeitsch. physiol. Chem.*, 1913, 87, 171—181).—The blood serum is centrifuged and examined in a layer of 4 cm. in a spectro-scope. The thickness of the layer is then diminished so as to locate the position of the absorption bands. The hæmatin is then converted by means of ammonium sulphide into hæmochromogen, and the spectrum again examined. The delicacy of the test depends on the transparency of the serum and the presence of other pigments. In some cases hæmatin corresponding in amount with a 1% solution of blood has been detected. E. F. A.

